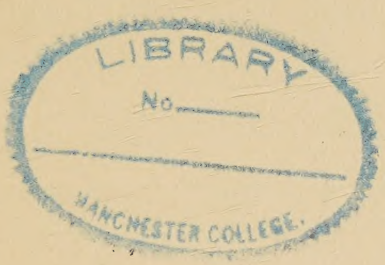
LIBRARY
MANCHESTER COLLEGE


LIBRARY
No.
MANCHESTER COLLEGE.

Digitized by the Internet Archive
in 2026

https://archive.org/details/technicalmethods0000wilf

# TECHNICAL METHODS
IN
# ANALYSIS OF METALLURGICAL
AND
# ALLIED PRODUCTS

A MANUAL OF ANALYTICAL METHODS AND USEFUL DATA FOR THE CHEMIST AND THE COLLEGE STUDENT

BY

WILFRED W. SCOTT, Sc.D.

ASSOCIATE PROFESSOR OF CHEMISTRY, COLORADO SCHOOL OF MINES
METALLURGICAL ANALYSIS, INDUSTRIAL RESEARCH AND CHEMICAL ENGINEERING
FORMERLY CHIEF CHEMIST, BALDWIN LOCOMOTIVE WORKS
RESEARCH CHEMIST, CHEMICAL ENGINEER, GENERAL CHEMICAL COMPANY
AUTHOR OF "QUALITATIVE CHEMICAL ANALYSIS"
"STANDARD METHODS OF CHEMICAL ANALYSIS," ETC.

---

IN COLLABORATION WITH EMINENT SPECIALISTS

---

**150 Illustrations and 2 Colored Plates**

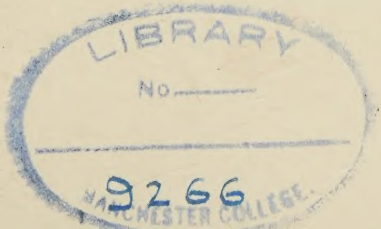
NEW YORK
D. VAN NOSTRAND COMPANY
EIGHT WARREN STREET
1923

COPYRIGHT 1923, BY
D. VAN NOSTRAND COMPANY

THE PLIMPTON PRESS
NORWOOD · MASS · U·S·A

Sco 86

THIS BOOK IS
AFFECTIONATELY DEDICATED
TO MY WIFE
HARRIET ELEANORA



# PREFACE

Although many excellent text books on metallurgical analysis have been published and are extensively used, no special effort has been made to compile a work to meet the demand of an academic text book for the student and a general reference work for the professional metallurgical chemist. The author has taken advantage of an experience extending over a period of twenty years, eight years as an intructor in chemistry and twelve years as a professional industrial chemist, to ascertain the requirements of a book suitable for an academic laboratory and the industrial plant.

It is manifest that no one individual can claim equal proficiency in the subjects with which this book deals; the author's work, therefore, is largely that of the editor in careful selection from the wealth of published information and the enlisting of specialists in direct contribution, or criticism of material selected. The latest edition of the author's work "Standard Methods of Chemical Analysis" has been freely consulted and many of the procedures appearing in this work have been used verbatim et literatim. In a great number of cases the general procedures have been modified, especially those methods designed for the instruction of the beginner. Suggestions are offered throughout the work that are designed to assist the instructor and student in making a selection of methods and the progressive order of this selection, but it is felt that the teacher is best able to judge the requirements of his students so that no attempt is made to dictate the course that should be followed.

The alphabetical arrangement adopted in Standard Methods of Chemical Analysis has been adopted in this book, as the author believes that this facilitates accessibility to information given. The introductory chapter has been written more for the student than for the professional, but it is believed that the subjects presented here will prove of value to those possessing a more extended experience in analytical chemistry.

Each chapter, dealing with the elements, has an introductory section devoted to the occurrence of the material in nature, and

brief descriptions of the important minerals in which each substance is found. The characteristics of the elements are given and the best methods by which they may be detected. Following this section are the procedures for decomposition and solution of materials in which the elements commonly occur, and methods of quantitative isolation. The general procedures now follow under classification of "Gravimetric Methods," "Volumetric Methods," "Industrial Products and Raw Materials" and methods for determining small amounts of the element. The procedures have been selected on account of their proven value for accuracy, ease of manipulation and rapidity.

In conclusion the author wishes to express his appreciation of the valuable assistance and cooperation of many, whose names appear throughout the book. The chapters on water analysis, analysis of gas, analysis of coal, fire assay of gold and silver, calibration of apparatus, methods of sampling, etc., have been contributed by men of broad experience in these subjects. Special mention is made of Dr. F. M. Van Tuyl, Professor of Geology, Colorado School of Mines, for his review and criticism of sections dealing with minerals; Prof. I. A. Palmer, Department of Metallurgy (C. S. M.) for his review of the chapter on "Slag Analysis"; Prof. A. H. Low, Department of Chemistry, (C. S. M.) for many helpful suggestions; and Dr. F. E. Hale, Department of Water Supply, Gas, and Electricity, New York City, for his assistance in proof reading of the entire work.

WILFRED W. SCOTT.

Golden, Colorado
June, 1923.

# CONTENTS

## PART I

### INTRODUCTION

General processes of quantitative analysis; gravimetric methods, the precipitate, colloidal condition, precipitation of colloids, washing precipitates; volumetric methods, the end-point, indicators, acidimetric-alkalimetric or neutralization methods, rules for making of solutions of approximate strength without the use of balances, oxidation and reduction methods, electrometric methods, precipitation methods, colorimetric and stain processes. *Normal solutions*, normal equivalents and normality factors, table of equivalents, equivalents in acidimetry and alkalimetry, in oxidation and reduction processes; normality factor, normality factor by titration against a standard, standardization against a solid, equivalent from a second standard, examples in calculations, manganese, vanadium, molybdenum, potassium dichromate, iodimetry; standard reagent defined. Analytical procedures, difficulty of complete separation, limit of accuracy in analysis. Brief summary of some important chemical laws and hypotheses—Avogadro, Boyle, common ion, complex ions, conservation of mass, constant proportion, Dalton's atomic theory, Faraday, Guy–Lussac, Lavoisier–Leplace, mass action, multiple proportion, Neuman–Kopp, periodic law, reversible reaction, Coulumb, Joule, Ohm. General manipulations, sampling, preparation of the sample, solution of the sample and laboratory procedures—Sampling, unit, collection of gross sample, carload lots, carts, trays, cranes, buckets, etc.; ship loads, scows, etc., powdered material, wet material; apparatus used in sampling; hygroscopic materials, material from roasters, dryers, furnaces, non-ferrous metals and alloys, pigs, sheets, etc.; procedures for reducing the gross sample, cone and quartering; long pile and alternate shovel; apparatus for reduction and preparation of the sample, crushers, grinders and riffle samplers; mixing and dividing the sample, standard sieves; containers for shipment; drying ovens. Weighing, use of the balance, construction, notes on care of the balance; summary of rules for weighing, checking the weight. Solution — apparatus used in decompositions, Erlenmeyer and Low's flask, beaker, casserole; fusions; weight of sample required; decomposition of material. Minerals and ores and best solvents of the

same—carbonates, oxides, semi-metals, metals, silicates, sulphides, sulphates, native elements, alloys, steel. Reagents used as solvents —list of, liquids and solids, oxidizing and reducing agents. Precipitation—suggestion for making up reagents, method of conducting precipitations. Filtration—types of filters, filtering precipitates for ignition, preparation of the Gooch crucible, filtration and washing of precipitates. Ignition apparatus used, burners, the flame, electric furnace, crucibles; care of platinum; procedure in ignitions, the desiccator. Standardization of weights and volumetric apparatus. Precautions in volumetric analysis, reading burettes. Analysis—determination of moisture and water of crystallization in substances not decomposed by ordinary heat. Determination of moisture in gases. Suggestions for the instructor and student. Outline of subject treatment. Elementary course for beginners, advanced course in quantitative analysis, special courses. Demonstration method for laboratory instruction, illustration—manganese in ores, oxalic acid method. Keeping records. Pages 3 to 73 inclusive.

PART II

*ANALYTICAL METHODS*

ALUMINUM

Descriptive, occurrence, minerals—bauxite, cryolite, corundum, other minerals. Detection—general procedure tests with cobalt nitrate, sodium thiosulphate, alizarine. Suggestions for experimental work. Preparation and solution of the sample, separations. Gravimetric methods,—determination by hydrolysis of an aluminum salt with ammonia, decomposition of aluminum substances, separations and notes; precipitation of aluminum as phosphate. Industrial products and raw materials—colorimetric estimation of small amounts of aluminum; bauxite analysis—sampling, extraction of ores of aluminum for their commercial valuation, the insoluble residue, soluble alumina, soluble iron, silica, titanium oxide, iron and alumina. Volumetric determination of available alumina in bauxite and clays. Analysis of metallic aluminum—fusion method, graphitic silicon, iron; determination of aluminum in iron and steel. Pages 75 to 88.

ANTIMONY

Descriptive, occurrence, minerals—native antimony, stibnite, other minerals. Detection—general procedure, hydrogen sulphide test, min-

erals, hydrolysis, traces of antimony, distinction between antimony and arsenic salts. Suggestions for experimental work. Gravimetric methods. Volumetric methods—permanganate method, preparation and solution of the sample, separations from interfering substances. Antimony in alloys—potassium bromate method, standard solutions; iodine oxidation method. Industrial products and raw materials—antimony in solder metal and alloys. Determination of small amounts of antimony. Pages 89 to 96 inclusive.

ARSENIC

Descriptive, occurrence, minerals—arsenic, realgar, orpiment, arsenopyrite, white arsenic. Detection—hydrogen sulphide, volatility of chloride, traces by Gutzeit or Marsh test, distinction between arsenates and arsenites, comparison of Marsh tests for antimony and arsenic, dry tests. Suggestions for the student. Methods of Analysis—preparation and solution of the sample, industrial products, ores, oxide, fusion method, arsenic in sulphuric acid, lead arsenate. Preliminary considerations, isolation of arsenic by distillation as arsenous chloride, separation of arsenic from antimony by precipitation as sulphide in strong hydrochloric acid solution. Gravimetric method for arsenic—determination as a magnesium pyroarsenate. Volumetric methods for the determination of arsenic—oxidation with iodine, potassium iodate method. Determination of arsenic in ores—precipitation as sulphide. Determination of small amounts of arsenic by the modified Gutzeit method—preparation of reagents, preparation of the sample—acids, salts, procedure for making the test. Pages 97 to 114 inclusive.

BARIUM

Descriptive, occurrence, minerals—witherite, barite. Detection—as sulphate, as carbonate, as chromate, as fluosilicate, flame test, spectrum. Suggestions for students. Preparation and solution of the sample—ores, barium in insoluble residue, silicates, sulphides, carbonates, salts, organic matter. The alkaline earths—preliminary considerations, direct precipitation. Separations—from previous group elements, from alkaline earths—oxalate method, sulphate method, separation of alkaline earths from one another—barium from strontium and calcium, strontium from calcium, barium and strontium from calcium, barium from strontium. Methods for determining barium: Gravimetric methods—determination as sulphate, as chromate, solubility of chromate. Volumetric methods—titration with dichromate, titration with permanganate, potassium iodide method. Industrial products and raw materials—analysis of barites and witherite. Pages 115 to 130 inclusive.

**BISMUTH**

Descriptive, occurrence, minerals—bismuth, bismuthinite, bismite, bismutite. Detection—as sulphide, by reducing agents, blowpipe test. Gravimetric methods—Preparation and solution of the sample—ores and cinders, alloys, lead bullion. Separation from members of subsequent groups, separation from arsenic, antimony, tin, molybdenum, etc., separation from mercury, lead, copper and cadmium. Determination as the oxide, $Bi_2O_3$, determination as the basic chloride, BiOCl. Industrial products and raw materials—bismuth in lead bullion, in alloys, in ores and mattes. Cinchonine potassium iodide method for small amounts of bismuth. Pages 131 to 142 inclusive.

**BORON**

Descriptive, occurrence, minerals—borax, colemanite, ulexite, etc. Detection—flame test, borax bead, turmeric test. Gravimetric determination by distillation, as methyl borate and fixation by lime. Volumetric method by titration of boric acid, evaluation of borax, method of Chapin. Pages 143 to 152 inclusive.

**BROMINE**

Descriptive, occurrence. Detection—by silver nitrate, carbon disulphide or tetrachloride; bromates test of, barium chloride test, magenta test for bromine. Gravimetric methods—preparation and solution of the sample, precipitation of bromine as silver bromide, notes on separations. Volumetric methods—potassium iodide method for determining free bromine, chlorine method, Volhard's method. Pages 153 to 157 inclusive.

**CADMIUM**

Descriptive, occurrence, minerals—greenockite, cadmium oxide, octavite. Detection—Hydrogen sulphide test, blowpipe tests. Preparation and solution of the sample—ores, carbonates, alloys. Gravimetric methods—determination as sulphide, as sulphate, by electrolysis. Industrial products and raw materials—cadmium in spelter, notes on separations, from silica; from subsequent group elements; from arsenic, antimony and tin; from copper and mercury; from zinc. Pages 158 to 166 inclusive.

**CALCIUM**

Descriptive, occurrence, minerals—fluorite, calcite, dolomite, argonite, anhydrite, gypsum, etc. Detection—general procedure, flame test, spectrum. Rapid preliminary examination. Suggestions for the student. Gravimetric determination by precipitation as oxalate and

ignition to oxide, solution of the sample—separations and procedure of final precipitation, notes. Volumetric determination by titration of the oxalate with permanganate. Industrial products and raw materials—Portland cement analysis. Other methods. Pages 167 to 177 inclusive.

CARBON

Descriptive, occurrence, minerals—graphite, diamond varieties, etc. Detection—element, compounds—carbon dioxide, monoxide. Gravimetric methods—preparation and solution of the sample—iron, steel and alloys; organic matter. Separations—cupric potassium chloride method for iron and steel. Absorption apparatus. Carbon determination in steel—combustion method, apparatus, furnace and combustion tube, absorption apparatus, procedure. Stetser and Norton combustion train, method of operation. Graphitic carbon, in iron and steel. Combined carbon, indirect method, direct colorimetric method. Beneker's modification of Eggertz's method. Determination of carbon dioxide in carbonates—absorption method; by loss of weight, by hydrometer method of Barker. Volumetric methods—by absorption in barium hydroxide, by absorption in gas apparatus. Cyanogen—Detection of hydrocyanic acid. Volumetric methods for determining hydrocyanic acid—Liebig's method, Volhard's method. Complex compounds—hydroferro and hydroferri cyanides. Pages 178 to 200 inclusive.

CERIUM

Descriptive, occurrence, minerals. Detection, general method, peroxide test, hypochlorite test, fixed alkali test. Gravimetric estimation—isolation of cerium, separation from other rare earths, separation from thorium. Methods—ceric iodate method of Brinton and James; determination of cerium in Welsbach mantles. Table of separations of the rare earth oxalates by Owens. Pages 201 to 206 inclusive.

CHLORINE

Descriptive, occurrence. Detection—free chlorine, silver nitrate test, hydrochloric acid action on manganese dioxide and permanganate, detection of chloride in presence of bromide and iodide. Suggestion for the student. Gravimetric determination of chlorine—Preparation and solution of the sample, water-soluble chlorides, water-insoluble chlorides, silver chloride, chlorine in rocks, free chlorine, chlorine in ores and cinders, separations. Silver chloride method. Volumetric methods—silver thiocyanate or Volhard's method, silver chromate or Mohr's method. Industrial products and raw materials—chlorine

in bleaching powder, in cement, copper and copper ores, chlorine, bromine and iodine in a mixture. Pages 207 to 217 inclusive.

. CHROMIUM

Descriptive, occurrence, minerals—chromite, crocoite. Detection, general procedure, test by barium salt, lead, mercury or silver salt, hydrogen peroxide, reducing agents, ether. Methods for determining chromium—Preparation and solution of the sample, decomposition of refractory materials, materials high in silica, peroxide fusion of chrome iron ores, solution of iron and steel, separation of chromium, iron and aluminum. Gravimetric method by precipitation of the hydroxide and ignition to oxide. Volumetric methods—potassium iodide method, by reduction with ferrous salt and titration with dichromate or permanganate. Industrial products and raw materials—chromium in a water soluble chromate, in chromite, in steel. Small amounts of chromium by diphenyl carbazide method. Pages 218 to 229 inclusive.

COBALT

Descriptive, occurrence, minerals—linnaeite, smaltite, cobaltite. Detection—general procedure, sulphocyanate test, nitrite of potassium test. Gravimetric methods—Preparation and solution of the sample—general procedure for ores; metallic cobalt, nickel and alloys. Separation from other members of the ammonium sulphide group metals, from the hydrogen sulphide group and from the alkalies; from nickel and manganese. Precipitation of cobalt by nitroso-beta-naphthol, precipitation by electrolysis. Industrial products and raw materials—cobalt in metallic cobalt and ferro-cobalt, cobalt in steel, in ores and enamels. Pages 230 to 238.

COPPER

Descriptive, occurrence, minerals—native copper, chalcocite, bornite, chalcopyrite, tetrahedrite, cuprite, malachite, azurite. Detection—general method, flame test, wet tests—hydrogen sulphide, potassium ferrocyanide, cupric salts, metallic iron or zinc test. Suggestions for the student. Methods—preparation and solution of the sample—ores, sulphide and oxidized ores and matte, metals. Methods of isolation of copper, thiocyanate method, separation as metal. Deposition of copper by electrolysis—rapid methods, Heath's solonoid, deposition from nitric acid, from ammoniacal solution, rotating anode method; slow methods—small and large portion methods, notes and precautions. Volumetric methods—potassium iodide method, volumetric method for ores; ferrocyanide method for small amounts of copper, ammonia method. Industrial products and raw materials, copper in refined

copper, electrolytic and hydrogen sulphide methods, copper in blue vitriol, copper and lead in brass, copper in steel, cast iron and alloy steels. Pages 239 to 259.

FLUORINE

Descriptive, occurrence, minerals—fluorspar, cryolite, apatite. Detection—hanging drop test, etching test, black filter test. Methods for the determination of fluorine. Preparation and solution of the sample—valuation of fluorspar, perchloric acid method, calcium fluoride, silicious ores and slags, removal of silicic acid from fluorides. Gravimetric methods for the determination of fluorine—precipitation as calcium fluoride. Volumetric methods—Method of Norris modified, determination by formation of silicon tetrafluoride and absorption of the evolved gas by Offerman's method, colorimetric determination of fluorine by Steiger's and Merwin's method. Determination of traces of fluorine. Industrial products and raw materials, valuation of fluorspar, analysis of sodium fluoride. Pages 260 to 274 inclusive.

GLUCINUM (Berillium)

Descriptive, occurrence, minerals—beryl. Detection—general procedure. Solution of the sample and separation from interfering elements. Gravimetric determination of glucinum. Pages 275 to 277 inclusive.

GOLD

Descriptive, occurrence, minerals—native gold, tellurides. Detection—general procedure, detection in alloys, benzidine acetate tests, phenylhydrazine acetate test, Dowsett's factory tests of barren cyanide solutions. Solubility. Gravimetric methods—wet gold assay of minerals, electrolytic method. Volumetric methods—preparation of the sample, permanganate method. Colorimetric methods—Priester's method, Cassel's method, Moir's method. Pages 278 to 286 inclusive.

HYDROGEN

Descriptive, occurrence. Determination of hydrogen in steel. Pages 287 to 289 inclusive.

IODINE

Descriptive, occurrence. Detection—the element, free iodine, iodide, iodate. Suggestion for students. Gravimetric methods—preparation of the sample, precipitation as silver iodide, palladous iodide method. Volumetric methods, determination in soluble iodides, decomposition of the iodide by ferric salts, decomposition with nitrous acid by the method of Fresenius, Volhard's method. Industrial products and raw

materials, determination of iodine in mineral waters and brines. Pages 290 to 296 inclusive.

IRIDIUM

Descriptive, occurrence. Detection, caustic alkalies, potassium chloride, ammonium chloride, hydrogen sulphide, metallic zinc, etc. Methods for determining iridium, preparation and solution of the sample, separation from platinum. Gravimetric methods—reduction with zinc, ignition of the ammonium salt, obtaining iridium as a residue. Pages 297 to 300 inclusive.

IRON

Descriptive, occurrence, minerals—oxides, native iron, pyrrhotite, pyrite, marcasite, hematite, magnetite, limonite, siderite, other minerals. Detection, ferric iron, tests with—hydrochloric acid, sulpho cyanate, ferrocyanide, salicylic acid; ferricyanide test for ferrous iron, distinction between ferrous and ferric salts, precipitation as hydroxide, sodium peroxide test. Suggestion for students. Methods—preparation and solution of the sample, soluble salts, ores, sulphides, ores with organic matter, oxides and roasted ores, silicates; fusions with potassium bisulphate, sodium carbonate; iron and steel. Isolation of iron—general procedure, special cases, ether method. Gravimetric procedures—precipitation as hydroxide, precipitation with cupferron. Volumetric methods—oxidation procedures after reduction with hydrogen sulphide, stannous chloride, a metal—test lead, zinc, etc., sulphurous acid, potassium iodide. Reagents—potassium dichromate, permanganate. Potassium dichromate method, optional dichromate method, potassium permanganate method, Jones' reductor, optional method for iron in ores. Reduction method for determining ferric iron using stannous chloride. Colorimetric method for small amounts of iron. Industrial products and raw materials. Technical analysis of iron and steel—Introductory, preparation of the sample, determination of carbon, combined by colorimetric method, total carbon by combustion, graphite in steel; manganese by ammonium persulphate method, lead oxide procedure of Deshey, bismuthate method; determination of phosphorus; determination of sulphur,—by evolution method, gravimetric method; determination of silicon. Pages 301 to 335.

LEAD

Descriptive, occurrence, minerals—native lead, galenite, cerussite, anglesite, pyromorphite, other minerals. Suggestions to students. Detection—general procedure, by potassium chromate, by sulphuric acid, hydrogen sulphide, sodium carbonate, zinc, dry tests. Methods

—preparation and solution of the sample—ores, oxides, sulphides, silicates and slags, alloys. Methods of isolation—separation as sulphate, ammonium acetate extraction. Gravimetric procedures—as lead sulphate, as chromate, as molybdate. Volumetric methods—chromate-iodide method, molybdate method, permanganate method. Industrial products and raw materials—complete analysis of pig lead. Determination of small amounts of lead—gravimetric method, colorimetric method. Pages 336 to 358.

MAGNESIUM

Descriptive, occurrence, minerals—dolomite, brucite, magnesite, other minerals. Detection—general procedure, barita or lime water, alkali bicarbonates, reduction action. Methods—preparation and solution of the sample, general procedure for ores, removal of impurities and isolation of magnesium. Hints for the student. Gravimetric method—precipitation as ammonium magnesium phosphate. Volumetric method—titration of phosphate with standard acid. Pages 359 to 366.

MANGANESE

Descriptive, occurrence, minerals—braunite, pyrolusite, manganite, rhodochrosite, other minerals. Suggestion to students. Detection—general procedure, manganese in soils, minerals, etc., borax and fusion tests. Methods—preparation and solution of the sample, ores, alloys, separation from interfering elements, basic acetate method, separation as manganese dioxide. Gravimetric method by determination as pyrophosphate. Volumetric methods—bismuthate method, notes; Volhard's method; ammonium persulphate method. Industrial products and raw materials—analysis of spiegel iron, oxalate method (reference). Pages 367 to 380.

MERCURY

Descriptive, occurrence, minerals—native mercury, cinnabar, calomel, other minerals. Detection—general procedure. Gravimetric methods—preparation of the sample, ammonium sulphide method, electrolytic method, Holloway-Eschka method. Volumetric method of Seamon. Pages 381 to 386.

MOLYBDENUM

Descriptive, occurrence, minerals—molybdenite, molybdite, wulfenite. Detection—general procedure, by sodium thiosulphate, by sulphur dioxide, other tests. Preparation and solution of the sample, general procedure—acid and fusion methods, molybdenum in steel. Gravi-

metric method by precipitation as lead molybdate. Volumetric methods—Jones' reductor-permanganate method. Industrial products and raw materials—wulfenite or molybdenite analysis, molybdenum and vanadium in the same solution. Pages 387 to 397.

NICKEL

Descriptive, occurrence, minerals—millerite, niccolite, garnierite, other minerals. Detection—general, by dimethylglyoxime, alpha benzildioxime Methods—preparation and solution of the sample—general procedure for ores, fusion methods, solution of nickel and alloys. Gravimetric determination by dimethylglyoxime, precipitation by electrolysis. Volumetric potassium cyanide method. Industrial products and raw materials—nickel in alloys, in nickel plating solutions. Pages 398 to 409.

NITROGEN

Descriptive, occurrence, element, air, free, total and combined. Detection, element, organic nitrogen, in gas, ammonia, salts, nitric acid, diphenylamine and copper tests, nitrous acid, permanganate test, nitrate in a nitrite salt. Procedures for the determination of combined nitrogen-ammonia by gravimetric method as platinochloride salt; nitric acid and nitrates by gravimetric procedure as nitron nitrate. Nitrogen in soil extracts,—Vamari-Mitscherlich-Devarda method. Determination of nitrogen nitrates by nitrometer method. Nitrites by Buovold's method, volumetric permanganate method. Pages 410 to 420.

OSMIUM

Descriptive. Detection—general procedure, hydrogen sulphide, sodium sulphite, phosphorus, mercury, stannous chloride. Gravimetric method. Pages 421 to 424.

OXYGEN

Properties and occurrence. Determination of oxygen in steel. Determination of free oxygen in gas—phosphorus and pyrogallate methods. Pages 425 to 428.

PALLADIUM

Descriptive. Detection, general procedure, by alkalies, ammonia, sulphur dioxide, cuprous chloride, mercuric cyanide, potassium iodide, etc. Gravimetric methods—preparation and solution of the sample, separations from platinum, iridium, silver and gold. Methods—gravimetric. Pages 429 to 432.

PHOSPHORUS

Descriptive, occurrence, minerals—apatite, wavellite, wagnerite, vivianite; typical analyses of bone ash and phosphate rocks. Detection—element, acids; comparison of ortho, meta and pyrophosphoric acids. Methods of analysis, preliminary remarks, preparation and solution of the sample, iron ores, phosphate rock and minerals; iron and steel, ores containing titanium. Gravimetric methods—precipitation of ammonium phosphomolybdate, determination as magnesium pyrophosphate. Volumetric methods—alkalimetric method, method for copper alloys, method for steel; zinc reduction and titration with potassium permanganate; determination of free phosphoric acid. Pages 433 to 447.

PLATINUM

Descriptive, occurrence, minerals—native platinum, sperrylite, alloys. Detection, reagent tests. Methods of analysis—preparation and solution of the sample, ores, platinum scrap, platinum in iron scale; separation from gold, iridium, palladium, ruthenium, rhodium and osmium. Gravimetric methods—weighing as metal, as salt, as metal by electrolysis. Industrial products and raw materials—assay of platinum ores, platinum and palladium in refined silver, copper anode slimes, platinum and palladium in gold. Pages 448 to 459.

POTASSIUM, SODIUM and OTHER ALKALIES

Descriptive. Potassium—occurrence, minerals. Detection—general procedure, detection of alkali hydroxides and carbonates. Preparation and solution of the sample—rocks and insoluble mineral products, soils, fertilizers, plant ash, saline residues and brines. Separation of the alkali metals from other constituents—iron, aluminum, chromium, etc., the alkaline earths, from boric acid, from magnesium by barium hydroxide and ammonium phosphate methods; separation of the alkalies from one another. Methods—modified chlorplatinate method, the chlorplatinate, Lindo-Glading method, the perchlorate method. Pages 460 to 469.

*Sodium.* Occurrence, minerals—halite, borax, cryolite, soda nitre, etc. Detection, general procedure. Preparation and solution of the sample. Methods—determination as chloride, determination as sulphate, determination by difference. J. Lawrence Smith method for alkalies in silicates, hydrofluoric acid method. Pages 470 to 475.

*Lithium.* Occurrence, minerals—spodumene, lepidolite, amblygonite, etc. Detection—general procedure. Methods—Gooch method, Rammelsberg method, determination as chloride, as sulphate, spectroscopic method. Combinations—sodium potassium and lithium; sodium and

potassium by indirect method; magnesium, sodium and potassium. Pages 476 to 480.
*Rubidium and Caesium.* Occurrence. Detection. Page 481.

### RADIUM

Descriptive, detection. Estimation—the alpha ray method; emanation method—example and calculation by carbonate fusion, bisulphate fusion; the gamma ray method. Methods for solution. Table of radium recovery. Pages 482 to 491.

### RHODIUM

Descriptive. Detection by special reagents. Methods of analysis —preparation and solution of the sample. Separation from platinum, iridium, palladium, ruthenium. Gravimetric method. Pages 492 to 494.

### RUTHENIUM

Descriptive, detection by special reagents. Methods of analysis —preparation and solution of the sample, separations from platinum, iridium, rhodium and osmium. Gravimetric method for determining ruthenium. Pages 495 to 498.

### SELENIUM and TELLURIUM

Descriptive, occurrence. Detection—general, detection of selenium, detection of tellurium. Methods of analysis—preparation and solution of the sample—selenium, tellurium, fusion method; separation of selenium and tellurium from the iron and zinc groups, from the alkaline earths and alkalies, from silver and from gold. Gravimetric methods—selenium precipitation with sulphur dioxide, reduction to metallic selenium by potassium iodide method. Tellurium—determination of tellurium, determination where selenium is not desired. Industrial products and raw materials—commercial selenium, tellurium. Pages 499 to 507.

### SILICON

Descriptive, occurrence, minerals of silica—silicates undecomposed by acids, silicates decomposed by acids. Detection—general procedure. Methods—preparation and solution of the sample—general considerations, procedure for decomposition of silicates not decomposed by acids, carbonate fusion. Procedure for the determination of silicon and silica, estimation of true silica. Industrial products and raw materials—

analysis of silicate of soda, analysis of sand for commercial valuation. Pages 508 to 516.

SILVER

Descriptive, occurrence, minerals—native silver, argentite, hessite, proustite, pyrargyrite, cerargyrite, other minerals. Suggestion to students. Detection of silver—wet method as chloride, other tests. Gravimetric methods—as silver chloride, as silver cyanide, electrolytic methods—Volhard's thiocyanate method, Guy-Lussac method, apparatus for the same, Denver Mint method. Pages 517 to 530.

STRONTIUM

Descriptive, occurrence, minerals—strontianite, celestite. Detection,—sulphate test, flame test, spectrum. Methods of analysis—preparation and solution of the sample; separation from magnesium and the alkalies, from calcium, from barium. Gravimetric methods—determination as sulphate, as oxide. Volumetric alkalimetric method. Pages 531 to 535.

SULPHUR

Descriptive—element, sulphur dioxide, hydrogen sulphide, sulphide and sulphate ores. Detection—element, sulphides, sulphates, sulphites, thiosulphates. Methods of analysis, preparation and solution of the sample, element, sulphide, sulphate, thiosulphate, sulphite; decomposition of sulphur ores, fusion method; sulphur in rocks, silicates, insoluble sulphates; Eschka's method for sulphur in coal; water soluble salts; substances containing iron. Separation from metals forming insoluble sulphates, from nitrates, chlorates, silica, ammonium and alkali salts. Gravimetric determination by precipitation as barium sulphate from hot solution, precipitation from large volume in cold solution, notes and precautions. Evolution method for determining sulphur in iron, steel, ores, cinders and metallurgical products. Free sulphur in a mixture. Industrial products and raw materials—brimstone, sulphuric acid gases, sulphur dioxide in burner and contact gases. Scott's gas analysis apparatus. Pages 536 to 558.

TANTALUM and COLUMBIUM

Descriptive, occurrence, columbite and other minerals. Detection—general procedure. Methods of analysis—preparation and solution of the sample—tantaliferous minerals, isolation of columbium and tantalum oxides, removal of tin, antimony and silica; separation of columbium and tantalum, by the selenium oxychloride method. Pages 559 to 563.

## THORIUM

Descriptive, occurrence. Detection. Preparation and solution of the sample—silicates, phosphates, oxides. Gravimetric method; minute amounts of thorium by Jolly's method. Thorium in monazite sand. Pages 564 to 570.

## TIN

Descriptive, occurrence, minerals—stannite, cassiterite. Detection—general procedure. Gravimetric methods—preparation and solution of the sample—assay of tin by cyanide process, sodium carbonate method, notes on separations. Gravimetric determination of tin in alloys. Volumetric determination of tin—iodide method of Lessen-Baker. The Sellar's apparatus for tin determination. Volumetric method for tin in alloys. Industrial products and raw materials—bichloride of tin—stannic acid method, Acker process method, bichloride of tin determined as sulphide. Pages 571 to 585.

## TITANIUM

Descriptive, occurrence, minerals—rutile and other minerals. Detection—hydrogen peroxide, morphine, zinc, sulphur dioxide tests, bead test on charcoal. Methods—preparation and solution of the sample—element, oxides, salts, steel, alloys, ores, titaniferous slags; separations from interfering substances—copper, zinc, aluminum, iron, alkaline earths, etc. Gravimetric methods—modified Gooch method, determination in ferro-carbon titanium. Volumetric methods—ferric-permanganate method, ferric method; colorimetric hydrogen peroxide method. Industrial products and raw materials—titaniferous ores—determination of titanium, determination of iron in presence of titanium, determination of silicon, aluminum, phosphorus; analysis of titanium pigments. Pages 586 to 601.

## TUNGSTEN

Descriptive, occurrence, minerals—wolframite, scheelite. Suggestion to students. Detection—minerals, iron, steel and alloys. Methods of analysis—solution of the sample metal, oxides, acids, minerals; separation of tungsten from silica, tin, titanium. Gravimetric procedures—determination of tungsten in steel and alloys; optional method. Tungsten in tungsten metal and ferro-tungsten. Determination in ores and concentrates; aqua regia method of Watts; volumetric method. Pages 602 to 613.

URANIUM

Descriptive, occurrence—uraninite (pitchblend), carnotites and other minerals. Detection—uranous salts, uranyl salts; potassium ferrocyanide test, other tests. Methods of analysis—preparation and solution of the sample, solution of ores, carnotite. Gravimetric determination as the oxide (Low), glacial acetic acid method (Scott). Volumetric determination by reduction and oxidation. Pages 614 to 622.

VANADIUM

Descriptive, occurrence, minerals—patronite, vanadinite, roscoelite and other minerals. Detection—by sulphide, reducing agents, peroxide, ammonium chloride; comparison of vanadium and chromium salts, detection of vanadium in steel. Methods—preparation and solution of the sample—element, oxides, ores, general procedure for decomposition—high and low silica ores, alloys. Gravimetric method by precipitation as lead acetate. Volumetric procedures—permanganate method, by titration of $V_2O_4$ and $V_2O_2$. Vanadium in ores, mine and crude mill samples, optional method, lead acetate method. Determination more than one constituent in the same sample, i.e., Mo and Vi; V, As and Sb; V in steel; V and Cr in steel. Pages 623 to 635.

ZINC

Descriptive, occurrence, minerals—sphalerite, zincite, smithsonite, willemite, calamine, franklinite, zinc. Suggestion to students. Detection—general procedure, ferrocyanide test, blow pipe test. Methods—preparation and solution of the sample—solubility, salts, ores, preliminary procedure, moisture in pulp; general procedure, refractory materials, material with carbonaceous matter, material containing metallics; separation from interfering substances, iron, aluminum, manganese, cobalt and nickel. Gravimetric methods—weighing as oxide, as sulphate, as phosphate, electrolytic methods. Volumetric methods—ferrocyanide method with internal indicator, notes on method; rapid ferrocyanide method for ores. Industrial products and raw materials—zinc in zinc dust. Small amounts of zinc by colorimetric method. Pages 636 to 654.

ZIRCONIUM

Descriptive, occurrence, minerals—zircon. Detection—general procedures. Methods—preparation and solution of the sample—materials with large amount of silica, general method for minerals, oxides, etc. Gravimetric methods—salts, ores, determination as phosphate, conditions of accuracy; determination as oxide, determination as oxide in presence of iron oxide. Pages 655 to 659.

## PART III

### ACIDIMETRY AND ALKALIMETRY

Introductory, indicators, tables. Ultimate standards—preparation of pure sodium carbonate; preparation of standard acid—sulphuric acid, normal, fifth normal, tenth normal acids; standard hydrochloric acid, benzoic acid; standard caustic solution. Standard burettes, titration of acids and alkalies. Acids—methods of weighing, dilute and strong acids non-volatile and volatile; apparatus used in weighing acids—Lunge-Ray pipette, Dely tube, snake tube, Burkhard burette, glass bulb. Inorganic acids—analysis of muriatic acid determining acidity, sulphuric acid, specific gravity. Analysis of sulphuric acid. Alkalies—analysis of sodium hydroxide, total alkali, sodium hydroxide, sodium carbonate, strength of liquors by hydrometer test. Potassium hydroxide. Determination carbonate and bicarbonate in presence of each other. Analysis of aqua ammonia. Volumetric estimation of free acid in presence of iron salts. Pages 661 to 681.

### ALLOYS

Descriptive. Table outline of separations. Analysis of type metal, solution, lead, copper and iron, antimony, tin, arsenic. Analysis of brass and bronze, solution, tin, arsenic, antimony, lead, copper, iron and zinc. Copper and lead by electrolytic method. Pages 682 to 689.

### SLAG ANALYSIS

Introduction, composition of slags. Decomposition of sample—general reverberatory slag, chilled blast furnace slag, lime, iron. Other constituents of slag—alumina, manganese, zinc, magnesia, copper. Electrolytic and iodide methods for copper. Pages 690 to 696.

### THE FIRE ASSAY FOR GOLD AND SILVER

Definitions—fire assaying, metallurgical products. General outline—reagents, furnaces and equipment, the assay—ton system, sampling, balances and weights, the crucible assay; lead reduction with oxidized ores, with sulphide ores; amount of litharge, of carbonate, of borax glass; assay slags. Weighing and mixing the charge, fusing the charge, crucible charges. The scorification assay, cupellation, parting. The assay of bullion. The assay of gold and silver bullion; silver bullion or Doré bullion assay, lead ratio in cupellation; gold bullion assay, U.S. Mint method. The assay of cyanide solutions, evaporation in lead tray, the Chiddey method, special method of assay. Pages 697 to 718.

## METHODS FOR ANALYSIS OF COAL

Introduction, sampling, preparation of sample for analysis. Methods of analysis, moisture, ash, volatile combustible matter, volatile sulphur, turbedimetric table, fixed carbon, calorific value, calculation of B.t.u. standardization of the calorimeter. Determination of fusibility of coal ash. Conversion of percentages of constituents in a substance from one moisture basis to another, from dry to wet basis or vice versa. Pages 719 to 735.

## WATER ANALYSIS

Introduction. Mineral analysis—outline of procedure, silica, iron, aluminum, calcium, magnesium, sulphate, sodium and potassium, alkalinity, acidity, free carbonic acid, chlorine, ammonia and its compounds, hydrogen sulphide, oil, dissolved oxygen Winkler method, hardness. Methods of reporting and interpretation. Water softening, foaming and priming, corrosion, scale, irrigating waters. Hypothetical combinations. Pages 736 to 753.

## GAS ANALYSIS

Sampling, tubes, containers, measurement of gas in large quantities, wet meter, pitot tube, formula for calculating velocity, the orifice meter, the anemometer, the gas flow meter; measurement of gas in small quantities, the Hempel gas burette, separatory funnel and graduate. Analysis of gas mixtures, Orsat apparatus description and manipulation; determination of carbon dioxide, oxygen, carbon monoxide, hydrocarbons; accuracy, time required. Chimney and flue gases, carbonic acid indicators, determination of temperature; composition of coal, loss due to carbonic oxide, smoke. Producers and fuel gases, blast furnace gas. Mine gases. Electrolytic gases. Atmospheric air, moisture, carbon dioxide, ozone, carbon monoxide, bacteria. Calorific power of various gases table. Gas reagents. Pages 754 to 774.

## REAGENTS USED FOR PRECIPITATIONS AND VOLUMETRIC DETERMINATIONS

Introduction. Reagents—acetic acid (glacial), alcohol, alizarin S, ammonium acetate, ammonium carbonate, ammonium chloride, ammonium molybdate, ammonium nitrate, ammonium oxalate, ammonium phosphate, ammonium sulphate, ammonium sulphide, ammonium polysulphide, ammonium thiocyanate, arsenic, arsenite, antimony solution, barium chloride, barium hydroxide, alpha benzildioxime, benzidine hydrochloride, bromine, bismuth sol., calcium chloride,

calcium hydroxide, cinchonine, cinchonine potassium iodide, copper sulphate—alkaline tartrate sol., citric acid, caustic, Devarda's alloy, dimethyl—glyoxime, diphenyl carbazide, Fehling's sol., ferric chloride, cuprous chloride acid and ammoniacal, ferrous sulphate, hydrochloric acid, hydrogen peroxide, iodine sol., lead acetate, magnesia mixture, manganous sulphate, mercuric chloride, mercuric chloride paper, methyl red, nessler's sol., nitric acid, palladous chloride, paraffin, peroxide, potassium dichromate, potassium chromate, potassium ferri and ferrocyanide, potassium fluoride, potassium hydroxide, potassium iodide, potassium permanganate, potassium thiocyanate, potassium pyrogallate, sodium chloride, silver nitrate, silver (pure) sodium bismuthate, sodium carbonate, sodium hydroxide, (water and alcoholic sol.) sodium sulphide, sodium metabisulphite, sodium thiosulphate, sulphuric acid, stannous chloride, starch sol., preservatives of starch sol., tartrate sol., thymol sol., zinc (amalgamated). Preparation and uses of chemical indicators—methyl orange, phenolphthalein, rosolic acid, cochineal, phenacetolin, lacmoid, turmeric paper. Pages 775 to 799.

STANDARD LABORATORY APPARATUS

Volumetric apparatus—preparation of apparatus; stop-cock grease; measurement capacity—direct measurement, calculation from weight of water; flasks, burettes. Table of buoyancy constants, density table, table of apparent weight in air. Standardization of weights—introduction, standardization—first method, second method, adjustment of weights, third method, effect of buoyancy, precision and tolerance of weights. Pages 800 to 815.

INDEX . . . . . 853

REFERENCES . . . . . 851

# LIST OF ILLUSTRATIONS


| FIGURE | | PAGE |
|---|---|---|
| 1. | Apparatus for Sampling Solids | 24 |
| 2. | Method for Sampling Ores | 27 |
| 3. | Jaw and Toggle Crusher | 28 |
| 4. | Crusher and Grinder in Cross Section | 29 |
| 5. | Roll Grinder for Brittle Material | 30 |
| 6. | Roll Grinder with Case Lifted to Show Interior | 30 |
| 7,8,9,10. | Types of Grinders and Pulverizers | 31 |
| 11,12. | Riffle Samplers | 32 |
| 13,14. | Drying Ovens | 35 |
| 15. | Vacuum Drying Oven | 36 |
| 16. | Beam of an Analytical Balance | 37 |
| 17. | Scale Balance | 38 |
| 18. | Base of Balance Case | 38 |
| 19. | Analytical Balance | 39 |
| 19a. | Box of Weights | 41 |
| 20. | Beaker | 42 |
| 21. | Erlenmeyer Flask | 42 |
| 22. | Low's Flask | 42 |
| 23. | Casserole | 43 |
| 24,25,26,27. | Filtering Apparatus | 57 |
| 28. | Cone Filter | 58 |
| 29. | Paper Filter Showing Folding | 58 |
| 30. | Method of Filtering | 58 |
| 31. | Filtration with Gooch Crucible | 59 |
| 32. | Bunsen Burner | 61 |
| 33. | Meker Burner | 61 |
| 34. | Blast Lamp | 61 |
| 35. | Flame Showing Zones of Heat | 61 |
| 36. | Electric Furnace | 62 |
| 37. | Platinum Crucible | 62 |
| 38. | Porcelain Crucible | 62 |
| 39. | Pipestem Triangles | 63 |
| 40. | Desiccator | 64 |
| 41. | Method of Reading Burettes | 65 |
| 42. | Apparatus for Determining Moisture | 67 |
| 43. | Fitzpatrick Apparatus for Determining Traces of Antimony | 96 |

FIGURE PAGE
44. Knorr Arsenic Distillation Apparatus . . . . . 102
45. Purification of Hydrochloric Acid . . . . . 110
46. Gutzeit Apparatus for Arsenic Determination . . . . . 114
47. Distillation of Methyl Borate . . . . . 146
47b. Apparatus for Distillation of Boric Acid . . . . . 147
48. Distilling Apparatus for Boron . . . . . 150
49. Apparatus for Detection of Cadmium . . . . . 159
50. Apparatus to Test for Carbonate . . . . . 179
51. Chilled Steel Mortar . . . . . 180
52. Geissler Bulb . . . . . 181
53. Liebig Bulb . . . . . 181
54. Gerhardt Bulb . . . . . 181
55. Vanier Bottle . . . . . 182
56. Fleming's Apparatus for Determining Carbon by Combustion . 183
57. Fleming Absorption Apparatus . . . . . 184
58. Stetser and Norton Combustion Train for Carbon Determinations . . . . . 187
58a. Hutchinson-Weirick Combustion Bulb . . . . . 188
59. Boat and Holder for Carbon Determination . . . . . 189
60. Hot Water Rack for Test Tubes . . . . . 190
61. Carbon Tubes . . . . . 191
62. Color Comparator or Camera . . . . . 191
63. Apparatus for Determining Carbon Dioxide . . . . . 193
64. Schroetter's Alkalimeter . . . . . 194
65. Mohr's Alkalimeter . . . . . 194
66. Barker's Hydrometer . . . . . 196
67. Victor-Meyer Bulb . . . . . 197
68. Solenoid for the Rotation of the Electrolyte . . . . . 245
69 and 69a. Riffler Sampler . . . . . 248
70. Constant Temperature Bath and Dividing Pipette . . . . . 249
71. Hydrometer-jar-shaped glass . . . . . 250
72. 400 cc. Beaker . . . . . 257
73. Combustion Furnace, Hinged Type . . . . . 257
74. Hanging Drop Test for Fluorine . . . . . 260
75. Etching Test for Fluorine . . . . . 261
75a. Zeisse Binocular Microscope . . . . . 262
76. Fluorine Apparatus . . . . . 267
77. Fluorine Chart for Determining Percentage . . . . . 268
77a. Fluorine Chart, Ratio of Depths of Color . . . . . 269
78. Apparatus for Determining Traces of Fluorine . . . . . 271
78a. A Chessel Stop-cock Remover . . . . . 274
79. Apparatus for Determining Hydrogen in Steel . . . . . 287

FIGURE PAGE
80. Apparatus for Determining Leaks in Combustion Train . . . . 288
81. Apparatus for Determining Iodine . . . . . 295
82. Jones Reductor . . . . . 319
83. Apparatus for Stannous Chloride Titration of Iron . . . . . 322
84. Hurley's Colorimeter . . . . . 325
85. Dividing Pipette . . . . . 325
86. Duboscq Colorimeter . . . . . 358
87. Sulphur Extraction Apparatus . . . . . 383
88. Apparatus for Determining Mercury . . . . . 385
89. Reductor Tube . . . . . 393
90. Mitscherlich's Apparatus for Nitrogen Determination . . . . . 415
91. Davisson's Scrubber . . . . . 416
92. Nitrometer . . . . . 417
93. Apparatus for Determining Oxygen in Steel . . . . . 425
94. Gas Apparatus for Determination of Oxygen . . . . . 427
95. Explosion Pipette . . . . . 428
96. J. Lawrence Smith Apparatus for Determining Alkalies . . . . 473
97. Alpha Ray Instrument for Determining Radium . . . . . 482
98. Radium Determination Boat . . . . . 484
99. Apparatus for Determining Radium . . . . . 485
100. Radium Apparatus . . . . . 486
101. Radium Apparatus . . . . . 488
102. Gamma Ray Apparatus . . . . . 489
103. Apparatus for Detecting Silicon . . . . . 509
104. Guy-Lussac Apparatus for Determining Silver . . . . . 525
105. A 5 cc. Pipette, with 1 cc. graduated . . . . . 529
106. Method of Evaporating Sulphur, Decomposed, Materials . . . 544
107. Precipitation of Barium Sulphate, Apparatus for . . . . . 545
108. Apparatus for Filtering Barium Sulphate . . . . . 545
109. Scott's Apparatus for Determining Sulphur in Iron and Steel . 548
110. Ignition of Sulphur Compounds with Fixing Reagents . . . . 549
110a. New Standard Apparatus for Determining Sulphur in Iron and Steel by Evolution Method . . . . . 550
111. Sander's Extraction Apparatus . . . . . 552
112. Portable Reich Apparatus . . . . . 554
113. Scott's Gas Analysis Apparatus . . . . . 558
114. Sellars' Apparatus . . . . . 579
115. Apparatus for the Volumetric Determination of Tin in Alloys . . 581
116. Apparatus for Determining Zinc in Zinc Dust . . . . . 650
117. Chart for Volumetric Determination of Zinc . . . . . 652
118. Oven for Constant-Temperature . . . . . 664
119. Chamber Burette for Volumetric Analysis . . . . . 668

FIGURE PAGE
120. Burettes for Volumetric Analysis . . . . . 668
121. Lunge-Ray Pipette . . . . . 671
122. Dely Weighing Tube in Operation . . . . . 671
123. Snake Tube . . . . . 672
124. Burkhard Graduated Weighing Burette . . . . . 672
125. Hydrometer . . . . . 675
126. Oil Muffle Furnace . . . . . 699
127. Muffle Furnace . . . . . 700
128. Cross Section of Two-Muffle Assay Furnace . . . . . 701
129. Apparatus for Fire Assay — Moulds, Tongs, Pliers, Flask . . . 702
130. Apparatus for Fire Assay — Cupel, Muffle, Crucible, Scorifier 703
131. Assay Balance for Small Weights . . . . . 704
132. Apparatus for Quartering and Pulverizing Coal . . . . . 720
133. V. C. M. Apparatus — Coal Analysis . . . . . 722
134. Emerson Calorimeter and Accessories . . . . . 727
135. Hoskins Electric Furnace, Optical Pyrometer . . . . . 732
135a, b, c. Apparatus for Coal Analysis . . . . . 735
135d. Platinum Evaporating Dish . . . . . 736
136. Gas Sampling Apparatus . . . . . 754
137. Gas Sampling Funnel Flask . . . . . 755
137a. Ozone Co. Laboratory Unit . . . . . 756
138. The Pitot Tube for Measuring Gas Flow . . . . . 757
139. Gas Flow Meter . . . . . 758
140. Elliott Gas Burette . . . . . 759
141. Orsat Gas Apparatus . . . . . 760
142. Sling Psychrometer . . . . . 769
143. Water Vapor Tension Chart . . . . . 769
144. Carbon Dioxide Absorption Apparatus . . . . . 770
145. Wolff Absorption Tube . . . . . 772
146. Blood Spectra in Testing for Carbon Monoxide . . . . . 772
147. Hydrogen Sulphide Gas Generating Apparatus . . . . . 783
148. Volumetric Measuring Apparatus . . . . . 801
149. Morse-Blalock Apparatus for Calibrating Flasks . . . . . 804
150. Volumetric Calibrating Apparatus . . . . . 806

PLATE I. Arsenic Stains, Gutzeit Method . . . . . *to face page* 109
PLATE II. Emissions — Spectra . . . . . " " 116

# TECHNICAL METHODS
IN
# ANALYSIS OF METALLURGICAL
AND
# ALLIED PRODUCTS

# INTRODUCTION

## GENERAL PROCESSES OF QUANTITATIVE ANALYSIS

§ 1. 1. Quantitative methods of chemical analysis may be classified under two general divisions — gravimetric and volumetric methods.

### GRAVIMETRIC METHODS

2. In gravimetric methods of analysis the substance sought is separated from solution either electrolytically as a metal or definite compound, or it is precipitated by means of a reagent in a form that may be separated readily from the mother liquor, dried and ignited either as an anhydrous salt or an oxide of definite composition.

*Examples:*

(*a*) Electrolysis — $CuSO_4$ solution = $H_2SO_4 + Cu\downarrow$ (metallic)

(*b*) Precipitation $BaCl_2 + H_2SO_4 = 2HCl + BaSO_4\downarrow$ (stable compound)

(*c*) Precipitation $CaCl_2 + (NH_4)_2C_2O_4 = 2NH_4Cl + CaC_2O_4\downarrow$ (unstable)

$CaC_2O_4$ decomposing with heat in presence of O $= 2CO_2\uparrow + CaO$ (stable compound)

3. It is essential that the compound precipitated should be insoluble in the mother liquor and also in the wash solution to be used. It should settle readily and be easily filtered and washed. It should be a pure, non-volatile compound of known definite composition, and should yield upon ignition a non-volatile compound of known percentage composition. A precipitate is specially desired which contains a low percentage of the substance sought, since this is conducive to accuracy.

§ 2. **The Precipitate.** — This may be fine or coarse grained. To prevent the material passing through the filter it is desirable to have the crystals coarse or as large as possible. The large grained crystals are induced by precipitating in a hot solution with slow addition of the precipitating reagent, and by allowing the precipitate to stand or *"digest" for some time.* The minute crystals, owing to their greater exposed surface, dissolve more readily than the larger crystals, the solution becomes saturated in respect to the larger crystals and a deposit of material occurs on their surface. This deposition makes the solution unsaturated with respect to the smaller crystals and more of these dissolve. The process continues until the minute crystals have dissolved, their mass being added to the larger crystals. Stirring hastens the solution of the small crystals, since it brings fresh liquid constantly in contact and removes the saturated. *Heating is of special value in case of extremely insoluble crystals* such as barium sulphate, though under certain conditions, extreme dilution, large crystals of this compound

are produced in the cold (see chapter on sulphur). *Supersaturation is undesirable* in precipitation and may be *largely avoided by slow addition of the precipitating reagent,* the solution thus being given time to deposit its excess as far as possible on the first crystals. *Stirring* brings the older crystals in contact with all parts of the slightly supersaturated solution.

**§ 3. Colloidal Condition.** — 1. Under certain conditions a difficultly soluble substance may be produced in a solution without the separation of a precipitate and also without the formation of a supersaturated solution. We have an example of this in the yellow, opalescent solution of arsenious sulphide, formed by passing $H_2S$ into an arsenious solution. The colloid passes through the finest grained filter. Colloidal solutions of platinum, gold, silver, iron, arsenic and other metals are simply suspensions of solid particles in extremely fine division, or a perfect emulsion of difficultly miscible liquids.[1]

2. These colloidal particles have been found to carry electric charges so that there is a potential difference between the particles and the liquid in which they are suspended. Arsenious sulphide particles in the colloidal state are negative and the solution in which they are bathed is positive. Colloidal ferric hydroxide in water is positive, while the water is negative.

3. *Precipitation of Colloids.* — This may be accomplished by addition of electrolytes with oppositely charged ions; negatively charged colloids being precipitated by addition of positive ions and positively charged colloids by negative ions. [Hardy's rule. Proc. Royal Soc. *66,* 110 (1899.)] The precipitated colloid absorbs a part of the precipitating ions. A colloid may be precipitated by a colloid carrying the opposite charge. Thus ferric hydroxide, carrying a positive charge, will precipitate colloidal arsenious sulphide, carrying the opposite charge. In the presence of hydrochloric acid negatively charged colloidal gold is precipitated by the positively charged colloidal stannic acid.

4. The precipitating power of electrolytes increases with the valence of the precipitating ions. [H. Schulze's rule. J. für pract. Chem. *25,* 431 (1882)] Bivalent ions are more efficient than monovalent, trivalent than divalent, less amounts of the products with higher valence being required. Ammonium salts being monovalent, comparatively large amounts are required to prevent colloidal formation.

**§ 4. Washing Precipitates.** — The subject is dealt with under "Practical Considerations." In washing the precipitate, two things must be considered in addition to washing out the mother liquor and the excess of the reagent, i.e. prevention of solution of the precipitated compound and prevention of colloidal formation; repressing ionization by addition to the wash water of a substance which is volatile and has a common ion with that of the precipitate, and a product which is volatile and fulfills conditions given under § 3, (3).

[1] Colloidal gold particles are approximately 6 $\mu\mu$ to 60 $\mu\mu$ in diameter.

## VOLUMETRIC METHODS

§ 5. 1. In volumetric methods the quantity of the substance may be determined by adding to its solution, by means of a calibrated burette, a solution containing a known amount of reagent per cc. (standard reagent, see § 28) in sufficient quantity to completely react with the total amount of the substance in solution. In many cases an excess of the standard reagent is added and its excess determined by "back titration" with another standard reagent which combines with the first, but does not interfere with the product formed by the first. Addition of a standard solution is spoken of as "titration."

2. **The End-point.** — The exact moment when the desired reaction is complete is recognized by a sudden change of color in the solution (or by electrometric methods, see § 6, III.) This color change is produced:

(*a*) *By means of an added indicator* which reacts with the reagent at the moment when a trace of excess is added to the solution over that required to completely react with the substance titrated. In other words the reagent has a selective action, as it reacts with the indicator only when the compound titrated has been disposed of.

(*b*) *By means of an "external" indicator.* This is placed in a series of drops on a glazed surface, a tile with a number of pits or depressions, each holding about 0.2 cc. of liquid, or on a white sheet of paper dipped in paraffin. The reagent is added to the solution titrated until a drop of the mixture produces a color change with a drop on the indicator on the glazed surface. This is usually abrupt, so that the titration is conducted very cautiously at the end.

(*c*) *The reagent acts as its own indicator.* When the amount required for complete reaction has been added with a trace of excess the color of the reagent becomes evident. Examples of this are seen in the pink potassium permanganate and the yellow iodine reagents.

§ 6. Volumetric methods may be conveniently classified as follows:

I. *A. Acidimetric-Alkalimetric or Neutralization Methods.* — The procedures depend upon the neutralization reactions of acids and bases, an indicator being added to the solution titrated.

*Examples:*

Acidimetry $NaOH$ (sought) + $HCl$ (standard) = $H_2O + NaCl$

Alkalimetry $H_2SO_4$ " + $2NaOH$ " = $2H_2O + Na_2SO_4$

(*a*) Occasionally more than one indicator is required. For example in the titration of sodium carbonate we may have a mixture of $NaOH$ and $Na_2CO_3$. By adding phenolphthalein the color change takes place when the following reaction occurs:

Phenolphthalein. $(NaOH + HCl)$ and $(Na_2CO_3 + HCl) = (NaCl + H_2O)$ and $(NaHCO_3 + NaCl)$

Now methyl orange is added, $NaHCO_3 + HCl = NaCl + H_2O + CO_2$

It is thus possible to determine one or more constituents in a mixture by volumetric methods.

*B. Volumetric Solutions in Neutralization Methods. Methods for Making Solutions of Approximate Strength, without the Use of Balances.*

1. Frequently it is necessary to make up solutions of an approximate strength for use in making up standard solutions.

Unless the word volume is used, percent means percent by weight. For example a 50% solution of sulphuric acid contains 50 grams of sulphuric acid and 50 grams of water per 100 grams of solution.[1]

2. *To Make a Solution of a Required Strength without Weighing.*

**Rule.** — Acid Solutions.

(*a*) Find the specific gravity of the reagent to be used.

(*b*) From the tables in a chemical handbook ("D. Van Nostrand Chemical Annual," "Standard Methods of Chemical Analysis") find out the percentage of the compound corresponding to this specific gravity.

(*c*) The specific gravity in terms of grams is the weight of 1 cc.

(*d*) Multiply the specific gravity by $\frac{1}{100}$ of the percentage to find the weight of the compound in 1 cc. of the reagent.

(*e*) Calculate the cc. of the reagent required to give in grams the percentage required. For example if 50% solution is desired calculate cc. that contains 50 grams of the substance.

(*f*) Multiply cc. thus found by specific gravity (this gives the weight of the cc.) and subtract from 100 to obtain the water that is necessary to make up the total to 100 grams.

*Example.* — A 75% solution of sulphuric acid is desired.

(*a*) The specific gravity is found by the hydrometer to be 1.8.

(*b*) Looking up the sulphuric acid tables, the acid having a specific gravity of 1.8 is 87% sulphuric acid.

(*c*) 1 cc. weighs 1.8 grams.

(*d*) $1.8 \times (87 \div 100) = 1.602$ grams $H_2SO_4$ per cc.

(*e*) 1.602 grams $H_2SO_4$ requires 1 cc. of the lab. reagent hence 75 grams will require $(1 \times 75)$ divided by $1.602 = 46.8$ cc. of the reagent per 100 grams of new solution.

(*f*) $100 - (46.8 \times 1.8) = 15.76$ cc. of water required for 46.8 cc. of the reagent to make 100 grams of sulphuric acid of 75% strength.

If $a$ = % acid desired, $b$ = specific gravity of acid used and $c$ = the percent of the acid used divided by 100 then $100 - \frac{a}{b \times c}$ = water required per 100 grams, or multiple thereof. Substituting in above example $100 - \frac{75}{1.8 \times .87} = 5.76$.

[1] In making up solutions with solids the word "percentage" is often used loosely; for example, the reagent 50% sodium hydroxide is 50 grams of the solid dissolved in water and diluted to 100 cc, the water in NaOH is neglected. See chapter on Reagents.

3. *To Make a Solution of Approximate Normality without the Use of Balances.*

**Rule.** — (*a*) Calculate the grams of reagent necessary in 1000 cc.

(*b*) By procedure in 2, find out the cc. of the reagent necessary to obtain the grams desired.

(*c*) Measure out the cc. required into a 1000 cc. flask and make to volume.

*Example.* — Required to make an approximately normal solution of sulphuric acid from a laboratory reagent that contains 87% sulphuric acid, the gravity of the acid being 1.8.

(*a*) A normal solution contains 49.04 grams $H_2SO_4$ per liter.

(*b*) 49.04 grams requires $\frac{49.04}{1.8 \times .87} = 29.2 +$ cc.

(*c*) Dilute 29.2 cc. to 1000 cc.

II. *Oxidation and Reduction Methods.* — Compounds capable of being reduced or oxidized, changing their valence from higher to lower state or vice versa, are determined by these methods. The modern theory assumes that a substance that is oxidized has taken on positive or has lost negative charges by ions, while a reduced substance has taken on negative or lost positive charges. Compounds containing iron, manganese, chromium, copper, arsenic, antimony, molybdenum, sulphur, oxalates, etc., may be determined generally by oxidation and reduction methods.

*Examples.* — Oxidation $10FeO + 2KMnO_4 = K_2O.2MnO. + 5Fe_2O_3$

Here Fe″ is oxidized to Fe‴

Reduction $Fe_2O_3 + 2KI = 2I + K_2O + 2FeO$

Here Fe‴ is reduced to Fe″

III. *Electrometric Methods.*[1] — The possibility of following changes in ionic concentration by observing changes in potential difference between a suitable electrode and a solution has led to the use in analytical work of a number of titrations in which the end-points are located by observing changes in electromotive force. If a hydrogen electrode for acidimetric titrations, or a metallic electrode in the case of oxidation-reduction titrations, is placed in a solution being titrated the potential difference between the electrode and solution will rise or fall as the titration proceeds. The change in potential difference with increase in reagent added is a maximum at the end-point, which is therefore represented by a point of inflection in the curve expressing the relation between potential difference and amount of reagent added. The principles underlying these so-called "electrometric" titrations have been discussed by Hildebrand.

Hildebrand has also shown the applicability of electrometric methods in analysis, research and teaching. The electrometric method

[1] Bulletin 2. The Eppley Laboratory, Newport, R. I.

has been used to good advantage by Hostetter and Roberts in a number of otherwise difficult determinations of ferrous and ferric iron; by Robinson and Winter for the determination of arsenic and by Kelley and Bohn for the tritation of ferrocyanides with permanganate. Forbes and Bartlett have shown that in the titration of dichromic acid with ferrous sulphate the end-point could be located by balancing the potentiometer circuit and observing the action of the galvanometer. Kelley and his collaborators have based methods for the determination of chromium, vanadium and manganese in steel on this method of titration. Hendrixson has shown that hydriodic acid can be titrated electrometrically with permanganate in the presence of hydrochloric and hydrobromic acids, and that on the basis of this titration dichromic acid, iodic acid and silver can be determined. Electrometric methods have resulted in simplifying a number of long and difficult analyses.

IV. *Precipitation Methods.* — The compounds reacting produce well defined precipitates, that separate out and leave the solution clear, so that the point where no further precipitation occurs may be recognized. This end-point is often recognized by placing in the solution a substance or indicator, which produces a color change when all of the material sought has been precipitated from the solution.

*Examples:*

(*a*) Direct precipitation. $AgNO_3 + NaCl = NaNO_3 + AgCl \downarrow$
(*b*) Added indicator $AgNO_3 + KCNS$ with $FeCl_3 = KNO_3 + AgCNS \downarrow$ the indicator now reacts $FeCl_3 + 3KCNS = 3KCl + Fe(CNS)_3$ red.

V. *Colorimetric Processes.* — Certain substances dissolved in appropriate solvents, yield solutions showing a characteristic color, with an intensity in proportion to the concentration of the ions producing the color. By comparing this solution with one containing the same compound in a convenient, known amount, i.e. with a solution whose ion concentration is known in terms of added solid, it is possible to estimate the amount of compound in the unknown solution.

Colorimetric methods are generally employed for the determination of minute amounts of substances existing generally as impurities in substances under examination.

VI. *Colorimetric Comparison of Stains.* — An illustration of this process is given under the chapter on arsenic in the determination of traces of arsenic by the Gutzeit method. See subject.

The last of these processes is in a class by itself and does not properly belong under the head of volumetric methods. The stains simply indicate the weight of substance that is evolved as a gas due to the chemical action.

## NORMAL SOLUTIONS, NORMAL EQUIVALENTS NORMALITY FACTORS

§ 7. 1. (*a*) *Definition.* — A liter of solution containing in exact amount 1.008 gram of available hydrogen or 8 grams of available oxygen or the equivalent of these is spoken of as a normal solution.

(*b*) An equivalent is that weight in grams of the element, the acid, the base or the salt which chemically replaces, combines with or in some way brings into reaction one gram of hydrogen or eight grams of oxygen.

2. Examples of Chemical Equivalents.[1]

| *Substance* | *Formula*[2] | *At. or Mol. Wt.* | *Normal Equivalent.* | | *Reaction or Nature of Sub.* |
|---|---|---|---|---|---|
| Hydrogen | $H'$ | 1.008 | 1.008 g. | per l. | Standard |
| Oxygen | $O''$ | 16.00 | 8.00 | " | Standard |
| Ammonia | $NH_3'$ | 17.03 | 17.03 | " | Alkali base |
| Arsenic ($As_2O_3 \rightarrow As_2O_5$) | $As''$ | 74.96 | 37.48 | " | Element |
| Barium | $Ba''$ | 137.37 | 68.69 | " | Element |
| Calcium | $Ca''$ | 40.00 | 20.00 | " | Element |
| Chlorine | $Cl'$ | 35.46 | 35.46 | " | Element |
| Hydrochloric acid | $HCl'$ | 36.46 | 36.46 | " | Acid |
| Hydroxyl ion | $-OH'$ | 17.01 | 17.01 | | Base |
| Iodine | $I'$ | 126.92 | 126.92 | " | Oxidizer |
| Iron | $Fe'$ | 55.84 | 55.84 | " | Element |
| Manganese ($MnO \rightarrow MnO_2$) | $Mn''$ | 54.93 | 27.47[3] | " | Divalent |
| Manganese ($Mn_2O_2 \rightarrow Mn_2O_7$) | $Mn'''''$ | 54.93 | 10.99 | " | Pentavalent |
| Oxalic acid | $H_2C_2O_4''$ | 90.02 | 45.01 | " | Acid. Reducer |
| Potassium | $K'$ | 39.10 | 39.10 | " | Element |
| Potassium dichromate | $K_2Cr_2O_7''$ | 294.20 | 147.10 | " | Precipitation |
| Potassium dichromate | $K_2Cr_2O_7'''''''$ | 294.20 | 49.03 | " | Oxidizer |
| Potassium permanganate ($K_2O.2MnO.5O$) | $KMnO_4'''''$ | 158.03 | 31.61 | " | Oxidizer in acid sol. |
| Potassium permanganate ($K_2O.2MnO_2.3O$) | $KMnO_4''$ | 158.03 | 52.68[3] | " | Oxidizer in neutral or alkaline sol. |
| Sodium | $Na'$ | 23.00 | 23.00 | " | Element |
| Sodium chloride | $NaCl'$ | 58.46 | 58.46 | " | Salt |
| Sodium hydroxide | $NaOH'$ | 40.01 | 40.01 | " | Base |
| Sodium oxalate | $Na_2C_2O_4''$ | 134.00 | 67.00 | " | Reducer |
| Sodium thiosulphate | $Na_2S_2O_3.5H_2O'$ | 248.20 | 248.20 | " | Reducer |
| Sulphuric acid | $H_2SO_4''$ | 98.08 | 49.04 | " | Acid |
| Zinc | $Zn''$ | 65.37 | 32.69 | " | Element |

3. A glance at the above table shows that the equivalent weight does not mean necessarily the atomic or molecular weight. In order to obtain the equivalent weight we must know the nature of the reaction that takes place in replacing, combining with or bringing into reaction the hydrogen or oxygen equivalents. To make this important

[1] A more complete list is given in table VII in the latter portion of this book.

[2] The exponents signify the number of hydrogen equivalents per atom of the substance.

[3] See example (*a*).

principle of volumetric methods clear we will study a few concrete examples.

**§ 8. Normal Equivalents in Acidimetry and Alkalimetry.**

1. When a base, such as sodium hydroxide, is acted upon by an acid, for example hydrochloric acid, taking the molecular weights of the two reacting compounds in grams (gram molecular weights or gram mols.) we find that 40.01 grams of NaOH react with 36.46 grams of HCl, involving a reaction with one gram (actually 1.008 g.) of hydrogen as seen by the equation.

$$NaOH + HCl = NaCl + H_2O$$

Normal solutions of sodium hydroxide and hydrochloric acid, therefore, contain the gram molecular weights of NaOH and of HCl per liter in their respective solutions.

2. In the case of sulphuric acid we find that for every gram mol. of sulphuric acid there are two grams of available hydrogen; hence a normal solution of this acid would contain one half of its molecular weight, 49.04 grams of the acid combining with 40.01 grams of NaOH:

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$
$$98.08 \text{ g.} \quad 80 \text{ g.}$$

3. A normal solution of a base contains 17.01 grams of hydroxyl (– OH) ion. A normal solution of calcium hydroxide, $Ca(OH)_2$, therefore would contain one half of its gram molecular weight per liter.

4. The salt, sodium chloride, NaCl, is made up of the basic element sodium and the acidic element chlorine. In the first reaction above it is evident that sodium replaces hydrogen in the ratio of their atomic weights, i.e. 23 : 1. Since the molecule contains one sodium in NaCl its normal solution is obviously its molecular weight, 58.46.

5. Zinc in reacting with HCl displaces two hydrogens as shown in the following reaction

$$Zn + 2HCl = ZnCl_2 + H_2 \uparrow$$

Therefore a normal solution of zinc or its salts should contain per liter one half the atomic weight Zn or one half the molecular weight of the salt. At. Wt. Zn = 65.37, normal equivalent weight = 32.69.

6. Barium in reacting with an acid displaces two hydrogens or involves 2 grams of hydrogen per gram mol. of Ba. Hence a normal solution of barium would contain per liter one half of its gram atomic weight. In like manner a normal solution of a barium salt would contain one half of its gram molecular weight per liter of solution.

$$BaCl_2 + H_2SO_4 = 2HCl + BaSO_4 \downarrow$$

**§ 9. Oxidation and Reduction Reactions. Normal Equivalents.**

1. In oxidation and reduction reactions it is necessary to know the nature of the reaction caused by the compounds involved and a simple glance at the formula of an oxidizing or reducing agent will not aid us in estimating the amount of the reagent necessary to make a normal solu-

tion. For example potassium permanganate has two normality factors, $\frac{1}{5}$ of the molecular weight and $\frac{1}{3}$ of the molecular weight of $KMnO_4$ according to the conditions under which the compound is used.

2. The oxidation reaction of permanganate is made clear when we get in mind the following structural formula:

Action in acid solution $2KMnO_4 = K_2O.\ 2MnO.$ **5 O.**

Action in neutral or basic solution. $K_2O,\ 2MnO_2.$ **3 O.**

3. The first reaction is more commonly employed so that in making up a normal solution of potassium permanganate one fifth of its molecular weight per liter is taken. It is evident that one gram molecular weight of $KMnO_4$ involves the action of $2.5 \times 16 = 40$ grams of oxygen (2 mols., as shown above, being $5 \times 16$) and since by the definition of a normal solution 8 grams of available oxygen are required $\frac{1}{5}$ the molecular weight must be taken per liter to make a normal solution.

4. In the reaction with potassium dichromate we may have two conditions. The first in a solution containing no reducing reagent where $K_2Cr_2O_7$ is used as a precipitating reagent. For example in the precipitation of lead we have the following reaction:

$$2Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = 2KC_2H_3O_2 + 2H.C_2H_3O_2 + 2PbCrO_4 \downarrow$$

Two gram equivalents of hydrogen are involved; hence half the molecular weight of potassium dichromate per liter will make a normal solution of a precipitating reagent.

5. With a reducing agent present in the solution potassium dichromate acts in a decidedly different manner. The action is shown by examining its molecule which may be represented

$$K_2Cr_2O_7 = K_2O.Cr_2O_3.\ 3\ O$$

It is evident that for every gram molecular weight of $K_2Cr_2O_7$ (294.2) there are available three oxygens i.e. $3 \times 16 = 48$ grams of oxygen. Since 8 grams of available oxygen are required per liter we would have to take $\frac{1}{6}$ the gram molecular weight of $K_2Cr_2O_7$ (49.03) to make a normal solution since a gram mol. contains 6 times the quantity necessary. $(48 \div 8 = 6)$

6. In the volumetric determination of chromium it is oxidized to its higher valence and then reduced by a standard reducing agent. The action is shown by the following:

$$2CrO_3 + 6H = Cr_2O_3 + 3H_2O$$

Two chromiums bring into reaction 6H or its equivalent, hence Cr = 3H and its normal solution would contain $\frac{1}{2}$ its molecular weight i.e. $52/3 = 17.33$ g. per liter.

7. Sodium oxalate as a reducing agent involves one oxygen per molecule of oxalate i.e. 16 grams O per gram mole. (134 g.) $Na_2C_2O_4$. Hence its normal solution would contain $\frac{1}{2}$ its molecular weight per liter. $(134/2 = 67$ g.)

8. Iron is determined by titration with a standard oxidizing agent. Its normal equivalent has been given in the table as 55.84 which is

the same as its atomic weight. The reason for this is evident by the following reaction:

$$2FeO + O = Fe_2O_3$$

Two Fe involves one O or 16 grams oxygen per two molecules of iron. One molecule therefore requires 8 grams of oxygen per 55.84 grams iron. A normal solution of iron, therefore contains 55.84 grams.

9. It is evident that all compounds or elements have equivalent or combining values. If a normal solution of any suitable oxidizing agent is used in the determination of iron, each cc. of this reagent would be equivalent to 0.05584 grams of Fe. A N/10 oxidizing agent would titrate 0.005584 g. per cc. A N/5 oxidizing agent would titrate $0.005584 \times 2 = 0.011168$ g. Fe since N/5 is twice the strength of N/10. Expressed also as 0.2N and 0.1N.

If the reagent were a little stronger than N/10 say 0.125 N then each cc. would be equivalent to $0.005584 \times 0.125$ g. Fe.

§ 10. 1. **Normality Factor.** — The actual amount of a reagent present in a unit volume divided by the equivalent weight necessary in that volume to make a normal solution gives the normality factor of the reagent.

One cc. of a normal iron solution contains 0.05584 g. If the reagent contained 0.056 g. Fe its normality factor $= 0.056 \div 0.05584 = 1.003$ N.

2. **Rule.** — To obtain the amount of substance in a solution that has been titrated by a standard solution, multiply the equivalent of that substance in gram per cc. by the cc. of the reagent required, which in turn have been multiplied by the normality factor for that reagent.

3. *Examples.* — (*a*) A solution of iron required 50 cc. of a standard oxidizing reagent whose normality factor was 1.05 N. How much iron is present in the solution?

The iron equivalent of 1 cc. of a normal solution is 0.05584 g. $(0.05584 \times 50 \times 1.05) = 2.9316$ g. Fe.

(*b*) A solution of sodium oxalate required 50 cc. of a standard oxidizing agent whose normality factor was 1.05 N. How much sodium oxalate is present in the solution?

The sodium oxalate equivalent per cc. of normal solution = 0.067. $[0.067 \times (50 \times 1.05] = 3.5175$ g. $Na_2C_2O_4$.

§ 11. **Normality Factor by Titration Against a Standard.**

1. **Rule.** — Multiply the cc. of the standard reagent required in the titration by its normality factor and divide the result by the cc. of the unknown taken, the result is the normality factor of the unknown.

2. *Example.* — 60 cc. of sodium hydroxide solution required 50 cc. of standard sulphuric acid, whose normality factor was 1.25 N. What is the normality of the sodium hydroxide?

$$(50 \times 1.25) \div 60 = 1.04 \text{ N.}$$

**§ 12. Standardization Against a Solid.**

1. **Rule.** — Convert the weighed amount of pure solid into its equivalent value in cc. of normal solution by dividing this weight by the normal equivalent per one cc. of the compound. Divide the cc. of this resulting volume by the cc. of the reagent required in the titration; the result is the normality of the reagent being standardized.

2. *Example.* — Potassium permanganate is being standardized against solid sodium oxalate. 0.3 grams of $Na_2C_2O_4$ required 40 cc. of the permanganate, what is the normality of the permanganate?

0.3 divided by 0.067 = 4.478 cc.
4.478 divided by 40 = 0.112N or 1.12 N/10

**§ 13. To find the equivalent value of a standard reagent in terms of a substance to be titrated when its normality factor is not given but a factor is given for some substance against which the reagent was standardized.**

1. **Rule.** — Multiply the factor of the reagent by the conversion factor obtained by dividing the gram equivalent of the substance sought by the gram equivalent of the substance against which the reagent was standardized, the result will be factor desired.[1]

2. *Example.* — Very commonly potassium permanganate is standardized against iron and the iron factor alone is placed on the bottle. What would be the equivalent in terms of some other element which may be titrated by permanganate? We will consider several cases.

Suppose the iron factor is .0057 g. Fe per cc.

(*a*) Factor for manganese determined by Volhards method.

By this method the manganese in manganous form is converted to $MnO_2$ while the permanganate is reduced only part way, as would naturally be expected as its reduction could not go below $MnO_2$.

In neutral solution the action of $KMnO_4$ is seen by the formula $2KMnO_4 = K_2O.\ 2MnO_2.\ 3\ O$. In the case of iron titration in acid solution the $KMnO_4$ yields 5 O i.e. $2KMnO_4 = K_2O.\ 2MnO.\ 5\ O$, hence 1 cc. of the reagent in the oxidation of manganese is $\frac{3}{5}$ of its value in titrating iron. This fact must be considered in obtaining the conversion factor. In the action MnO is oxidized to $MnO_2$ therefore Mn = O = 16 g. O. An 8 g. O equivalent therefore would be half the atomic weight of Mn 54.93 divided by 2 = 27.47. The iron equivalent we learned is 55.84. 27.47 divided by 55.84 = 0.492. This would be the factor if the permanganate value as an oxidizer were the same for Fe and Mn, but since for manganese its oxidation value is $\frac{3}{5}$ the oxygen as in its oxidation of iron we must multiply 0.492 by $\frac{3}{5}$ = 0.2952, therefore multiplying the iron value of the permanganate by 0.2952 will give the manganese equivalent of the reagent. $0.0057 \times 0.2952 =$ .001683 g. Mn per cc.

(*b*) Factor for vanadium. Vanadium is titrated in an acid solution so that the manganese oxidation value is the same as it is for iron,

[1] See list of conversion factors, table XVIII, in the latter part of this book.

namely 5 available oxygens per 2 mols. of $KMnO_4$. In this case the corrective factor that was necessary in the example above is not necessary.

In the methods commonly employed for vanadium, the reduction being conducted with $SO_2$, or $FeSO_4$ or HCl, etc. $V_2O_5$ is reduced to $V_2O_4$. This reduced solution is now titrated with permanganate, whereupon the $V_2O_4$ is oxidized to $V_2O_5$. Hence $V_2$ = O (= 16 g. O) The atomic weight of vanadium in grams would involve the reaction of 8 grams of oxygen hence its normal equivalent is its atomic weight = 51. The conversion factor of iron to vanadium is therefore 51 divided by 55.84 = 0.9159.

The reagent above = 0.0057 × .9159 = .00522 V per cc.

(*c*) Factor for molybdenum. In the titration of molybdenum in acid solution the permanganate gives up 5 oxygens per 2 mols. just as in the case of the iron titration. No corrective factor is then required as it was in case (*a*). To obtain the molybdenum equivalent we must know what takes place in the titration of molybdenum. The higher oxide is reduced by zinc to $Mo_2O_3$. Potassium permanganate is now used and the $Mo_2O_3$ is oxidized to $Mo_2O_6$ or $2MoO_3$. Therefore 2Mo require 3O, 2Mo gram mols. require 48 g. O, Mo requires 24 g. O, Mo/3 requires 8 g. O, hence its normal equivalent would be $\frac{1}{3}$ its atomic weight. 96 divided by 3 = 32. Therefore 32 divided by 55.84 = 0.5713, the conversion factor of Fe to Mo. The reagent above therefore will titrate 0.0057 × 0.5713 = 0.003256 g. Mo per cc.

3. *The values may be worked out by calculating the normality of the reagent.* 1 cc. N Fe solution contains 0.05584 g. therefore 0.0057 = (0.0057 divided by 0.05584) = 0.102 × N or 1.02 × N/10

| | *Equivalents* | *Value per cc. N. sol.* | *Conversion Value in terms of above reagent* |
|---|---|---|---|
| (*a*) | Mn=27.47 | 0.02747×0.102 | (×2/3 corrective) = 1 cc.=0.00168 g. Mn |
| (*b*) | V =51 | 0.051 ×0.102 | 1 cc.=0.0052 g. V |
| (*c*) | Mo=32 | 0.032 ×0.102 | 1 cc.=0.00326 g. Mo |

§ **14.** 1. *Potassium Dichromate.* — As may be seen from the table showing normal equivalents potassium dichromate has two equivalents; one where the salt is used *as a precipitating reagent*, the other where it is used as an oxidizing reagent. In the first case $K_2Cr_2O_7$ involves a reaction causing a displacement of elements or compounds which are equivalent to 2H, hence the normal equivalent of the dichromate is half its molecular weight.

(*a*) $2BaCl_2 + K_2Cr_2O_7 + H_2O = 2BaCrO_4 + 2KCl + 2HCl$

(*b*) $2Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = 2PbCrO_4 + 2KC_2H_3O_2 + 2HC_2H_3O_2$

2. Potassium dichromate as an oxidizing reagent has three available oxygens per molecule, which may be represented graphically as follows: $K_2O.Cr_2O_3.3O$. Its normal equivalent is therefore $\frac{1}{6}$ its molecular weight ($3 \times 16$ divided by $8 = 6$).

The reagent is specially useful in the determination of iron. It is sometimes used as an adjunct to permanganate in the determination of substances in which the potassium permanganate titration could not be made alone owing to the presence of reduced iron which is first oxidized by potassium dichromate. Examples of this are found in the determination of chromium and vanadium in presence of iron. See methods in chapters on these subjects.

§ 15. 1. *Iodimetry.* — Iodimetric methods in volumetric analysis are extensively used since the procedures are rapid and extremely accurate. Starch in solution is generally used as an indicator. Its reaction with iodine is very sensitive, the characteristic blue color being produced.

2. Iodine acts as an oxidizing reagent by either displacing oxygen in water with the liberation of oxygen which oxidizes the reducing agent (which must be present to induce the reaction), or the iodine combines directly with the hydrogen or alkali in the substance.

(*a*) Indirect oxidation. $I_2 + H_2O$ (in presence of reducer) $2HI + O$

$$As_2O_3 + 2I_2 + 2H_2O = As_2O_5 + 4HI$$

(*b*) Direct combination. $I_2 + H_2S = 2HI + S$

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

It is evident from the above reaction that the iodine equivalent is its atomic weight (126.92).

§ 16. 1. *Sodium thiosulphate* is a reducing agent commonly employed in iodimetric titrations. The gram molecular weight of the salt is its normal equivalent as appears from the last of the reactions above. The laboratory reagent contains 5 molecules of water of crystallization $Na_2S_2O_3.5H_2O$, hence 248.2 grams of the salt are required, usually an excess of this is necessary as free water is often present. It is always necessary to standardize the thiosulphate solution against iodine on account of the uncertainty of the compound.

For further information regarding these commonly used reagents consult the chapter of "Preparation of Reagents." The discussion of the few preceding pages is by way of introduction to methods that are given throughout the work.

§ 17. **Standard Reagent.** — From the examples cited we are prepared to define a standard reagent as a solution[1] which contains a definite amount of substance used in quantitative methods, whose amount per cc. is either known or its equivalent in terms of a normality factor, or in terms of some other substance for the determination of which the reagent is used.

[1] Or a solid (as $Na_2C_2O_4$) whose composition is a constant.

## ANALYTICAL PROCEDURES

§ 18. 1. *Difficulty of Complete Separation of Elements.* — As the great majority of the substances with which the chemist is called upon to deal are complex rather than simple, a careful study of the separation of the elements is of the greatest importance. Only by the closest attention to details can success be attained in the analysis of complex substances. The importance of testing precipitates for impurities and the solution for unprecipitated portions of an element cannot be too strongly urged. Only in this manner can the accuracy of an analysis be assured.

2. *Limit of Accuracy in Analysis.* — If a complete analysis is made the sum of all the constituents must be very close to 100%. A summation which is within .5% can generally be obtained if the analysis is conducted with care and reliable methods are used. In general the analysis of an unknown substance should be conducted in duplicate. If the duplicate results do not agree within .2 or at most .3%, a third analysis should be made. As the error in many determinations may be 0.1%, it is unnecessary to calculate results to more than hundredths of per cent. As the error in each determination of the analysis of a given substance may be either plus or minus, the practice of dividing the difference between the summation and 100% among the various determinations is not justifiable.

It is in some cases possible to analyze a substance in such a manner that the results are accurate to the hundredth of a per cent. Such results may be computed to the .001 of a per cent. This practice is common in the analysis of metals. Large quantities of the metal are taken, so that considerable quantities of the impurities which are present in small amounts are obtained for determination. The results may then be accurate to the hundredth of a per cent. This does not imply a higher degree of accuracy in the determination of a given element than .1 of a per cent. For example, if iron were present in copper to the extent of .5%, a determination of the iron which is accurate to .01% of the impure copper would represent an error of $\frac{1}{50}$ of the amount of iron present in the copper. In giving the results of such analyses the percentage of the main constituent is obtained by difference, so that the summation is exactly 100%.

## BRIEF SUMMARY OF SOME IMPORTANT CHEMICAL LAWS AND HYPOTHESES

§ 19. 1. **Avogadro's Hypothesis.** — Equal volumes of all gases at the same pressure and temperature contain an equal number of molecules.

2. **Boyle's (or Mariotte's) Law.** — The volume of all gases at a constant temperature is inversely proportional to the pressure.

3. **Common Ion Effect — Repression of Ionization.** — Ionization is repressed by adding to the solution a salt which has a common ion with that of the solute.

4. **Complex Ions.** — These consist of a group of elements, possessing characteristics distinct from the elements of which they are composed. Example $K_4Fe(CN)_6$ ionized = $K_4$ and $Fe(CN)_6$. $KClO_3$ ionized = K and $ClO_3$.

5. **Conservation of Mass, Law of.** — The total weight of matter resulting from a combination or decomposition is always equal to the sum of the weights of the substances taking part in the reaction. In all chemical transformations mass remains constant.

6. **Constant Proportion, Law of.** — The elements combine with one another in absolutely fixed relative proportions by weight.

7. **Dalton's Atomic Theory.** — All matter consists of an aggregate of minute particles, or atoms, which are chemically indivisible.

8. **Dalton-Henry's Law.** — The pressure exerted by a mixture of gases occupying a given volume is equal to the sum of the separate pressures which the different gases would exert if they alone occupied the given volume. Every gas behaves with respect to its own particular properties just as if it alone was present.

9. **Dulong-Petit's Law.** — All elements in the solid state have the same atomic heat. That is, elements taken in proportion to their atomic weights require equal quantities of heat in order to be raised to the same temperature.

10. **Electrolytic Dissociation Theory of Arrhenius.** — All substances which form solutions capable of conducting an electric current, the electrolytes, exist in solution, in part at least, as dissociated ions, atoms or atomic groups, carrying a definite charge of electricity. Each positive ion (anion) involves the presence of a negative ion (cation) carrying an equivalent amount of electricity.

When two oppositely charged poles are placed in such a solution, the positively charged anode attracts the negative particles in the solution and repels the positive, while the negatively charged cathode attracts the positively charged particles and repels those negatively charged, a flow of electricity thus being produced.

11. **Electromotive or Potential Series.** — Metals placed in solution tend to pass from a free element to the ionic condition, the more positive elements will displace the less positive from their ionic con-

dition. See list of elements given in order of activity, in the table in the latter part of this volume.

12. **Faraday's Law.** — In equal periods of time a current of definite strength separates the ions from the solutions of electrolytes in quantities by weight, which stand in the same ratio to one another as their equivalent weights, i.e. their atomic weight divided by their valence.

The strength of an electric current can be measured by determining the weight of silver or copper deposited at the cathode in a given time from a solution of silver or copper, or by measuring the volume of hydrogen or oxygen produced from water by the action of the current.

13. **Gay-Lussac's Law (Charle's Law).** — At constant pressure, volumes of all gases increase on warming in the same proportion for every one degree. The coefficient of expansion is 1/273 (0.003665). That is to say, for 1° C increase in temperature the gas expands 1/273 of its volume. A volume of 273 cc. of gas at 0° C would become 274 cc. at 1° C.

14. **Hesse's Law Thermo Law of Conservation.** — The evolution of heat which accompanies a chemical process is always the same whether the process takes place in one step or whether it passes through a number of intermediate processes.

15. **Lavoisier-Leplace's Law.** — Every compound has a certain heat of formation which is equal to its heat of decomposition.

16. **Mass Action, Law of (Guldberg-Waage's Law).** — The speed of reaction between two substances in solution is directly proportional, at any moment, to the molar concentrations of these reacting substances in solution, and to a constant, which is characteristic of the chemical nature of the reacting components, and of the temperature.

17. **Multiple Proportion, Law of.** — If two elements combine in more than one proportion, the masses of the one which combine with a given mass of the other bear a simple rational relation to one another, i.e. are always a whole multiple of the lowest.

*Example:* $N_2O$, $N_2O_2$, $N_2O_3$, $N_2O_4$, $N_2O_5$: the five oxides of nitrogen.

18. **Neuman-Kopp's Law.**— Molecular heat corresponds to the sum of atomic heats of the elements which constitute the molecule.

19. **Osmotic Pressure.** — A substance in solution produces the osmotic pressure, at a given temperature, which it would exert, if it were contained as a gas, at the same temperature, in the volume occupied by the pure solvent of the solution.

20. **Periodic Law of Mendeleeff.** — The properties of the elements are periodic functions of their atomic weights.

21. **Reversible Reaction.** — Compounds in solution resulting from a chemical reaction in turn react forming the original compounds present. This reversibility is prevented by removal from solution of one of the resulting compounds, by formation of an insoluble compound,

which precipitates from solution, or by the formation of a gas which escapes. (See "Common Ion Effect.")

22. **Law of Electrostatic force. Coulomb's law.** —

$$F = \frac{1 q_1 q_2}{C d_2}$$

$F$ = force acting between two charged bodies.
$q_1$ and $q_2$ = quantities of electricity.
$C$ = specific inductive capacity or dielectric constant of the medium.
$d$ = distance between the two charged bodies.

23. **Law of Jule.** —

$$h = rc^2$$

$h$ = amount of heat evolved in a given time.
$r$ = resistance to the passage of the current.
$c$ = strength of the current.

24. **Ohm's law.** —

$$C = \frac{E}{R}$$

$C$ = strength of current
$E$ = electromotive force.
$R$ = resistance.

# GENERAL MANIPULATIONS, SAMPLING, PREPARATION OF THE SAMPLE, SOLUTION OF THE SAMPLE AND LABORATORY PROCEDURES

## SAMPLING[1]

### I. General Outline for Sampling Solids

**§ 20. Introduction.** — An accurate and uniform sampling procedure, applicable to all solid materials from the viewpoint of both producer and consumer, would necessitate the standardization of an infinite number of details, and probably result in a very cumbersome and impractical manipulation. It, therefore, appears advisable to first consider the various steps of the process of sampling, attempting their standardization and then applying this standardization to each particular product or group of related products.

The process of sampling is divided into three major operations:

1. The collection of the " gross " sample.
2. The reduction of the " gross " sample to a proper and convenient size for transportation to the laboratory.
3. The preparation of the sample for analysis.

These essential points and the accuracy with which they are performed determine the value of the subsequent analytical results. Experimental data and general mathematical deductions make it possible to standardize these operations with a fair degree of accuracy.

### II. Sampling Unit

The sampling unit may be defined as that portion of the material which is chosen in such a manner that there is a high probability that it will contain the different sized particles of the material in the proportion in which they occur in the entire bulk of the material. Providing there are no great uncontrollable irregularities in the material, the sampling unit, if taken under carefully prescribed conditions for each different class, should be properly representative of the material. However in order to obviate the necessity of specifying in great detail, and to guard against unforeseen sectional variations in the material, it is more expedient to select a number of sampling units, these depending upon the size of the shipment to be sampled, and combine these sampling units into one large sample called the " Gross Sample."

The character of the material, size of the various particles, uniformity of composition and the prominence of any one or more constituents are factors governing the determination of the amount to be taken as the sampling unit. Without considering a mathematical discussion of the modulus of precision of a condition which would be

[1] Standard Methods of Chemical Analysis — Scott. D. Van Nostrand Co.

impossible of duplication and in view of the experimental data compiled on the sampling of coal, it is safe to adopt, as the general sampling unit, an amount of material equal to approximately 500 times the weight of the largest particle. If this is impractical, due to the presence of very large particles, and the material cannot be reduced by passing it through a crusher, it will be necessary to reduce, by hand, the large particles at the various sampling points so that the correct proportion of large particles can be included in the sampling unit. In some cases, however, a different bulk of sampling unit will be found necessary.

### III. Collection of the Gross Sample

The amount of material to be included in the gross sample depends more upon the size of the individual particles than upon the size of the shipment since it is simply a multiple of the sampling unit. When the shipment is large and frequent sectional variations do not prevail, and it is being transferred by containers with a capacity approximately equal to the sampling unit, it is advisable to take the entire contents of a definite percentage of the containers as increments of the gross sample.

When the accumulated gross sample is too large to handle conveniently as a unit, it is permissible to reduce the gross sample in small sections by the standard procedure and subsequently combine the reduced portions in the correct ratio.

**1. From Carload Lots.**

(*a*) **When the Material is to be Unloaded from Flat-bottomed Cars.** — Divide the top surface of the car into eight equal areas and, from each of these sections, take approximately the equivalent of one sampling unit in the following manner: From a stable bank of the material, beginning from the bottom, take with a shovel, at regular and equal intervals from the bottom to the top of the bank, ten equal portions of the material as specified. Combine these sampling units for the gross sample.

The stable bank may be obtained:

(1) By digging down to the bottom of the car at the center of each section.

(2) As the center of each section of the car is reached during the ordinary process of unloading by shoveling or otherwise.

(*b*) **When the Material is Being Transferred from or to the Car by Means of Wheelbarrows, Tram-cars, Wagons, etc.** — Take the specified increment according to the material in question from a specified number of conveying containers. Combine these increments for the gross sample. When at any point a particle is encountered which is larger than the specified increment it should be broken down and a portion of it included in the sample.

(*c*) **When the Material is Dumped from a Hopper Car into a Hopper, Bin or Pile.** — Under these conditions, the sample is taken from the resulting cone-shaped pile by beginning at the bottom outer edge of the pile and taking the specified increment, according to the character of the material, every two feet on a straight line to the apex of the cone. This operation is repeated on each quadrant of the pile. The entire procedure is repeated after each car has been dumped and all increments combined for the gross sample.

2. **From Wheelbarrows, Barrels, Bags, Tram-Cars, Carts, Trays, etc.**

(*a*) From a specified number of containers, take the specified increment and combine them for the gross sample.

(*b*) Take the entire contents of every *n*th container and combine them for the gross sample.

(*c*) If the material is fairly uniform and composed of small particles, sample the container by taking ten equal specified increments uniformly distributed on two right angle diagonals across the surface of the container. Sample the specified number of containers in this way and combine the several portions for the gross sample.

3. **From Crane Buckets, Cars, Carts and Similar Containers, Chutes, etc.**

(*a*) If one container amounts to less than one sampling unit, take every 10th load and combine these for the gross sample.

(*b*) If one container amounts to approximately 1–3 sampling units, take every 20th load and combine these for the gross sample.

(*c*) If one container amounts to more than three sampling units, take every 50th load and combine these for the gross sample. Note: When very large shipments are being sampled by the above procedures very large gross samples will result which would be difficult or inconvenient to reduce to the laboratory sample. In this case the gross sample may be reduced periodically as follows: At regular intervals, representing a definite number of tons, the gross sample is quartered, one quarter reserved and three quarters returned to the main bulk. The total combined quarters thus reserved are mixed by shoveling into a cone-shaped pile and then further reduced by the Standard Procedure to the laboratory sample.

(*d*) When the material is composed of particles one inch or less in size, take a specified increment from every *n*th container.

(*e*) When the material is being dumped into a crusher from which it flows or is flowing, from a drying kiln or other process kiln, the material may be sampled by taking specified increments from the outflowing stream at stated regular intervals.

4. **From Shipholds, Scows, Hoppers, Hopper-cars, Bins, Storage Piles, etc.** — In this case the material may be sampled in any of several ways.

(*a*) According to the previous section 3, while loading or unloading.

(*b*) According to the section 1, for carloads while unloading or loading.

(*c*) While using material from a storage pile, daily or periodic samples may be taken as follows: On ten vertical lines from the bottom to the top of the face of the pile distributed at uniform distances across the face, take ten equal specified increments at equal distances from bottom to top. Combine these increments for the gross sample over any desired period.

5. **For Powdered Material.** — When the material is a fine powder or is composed chiefly of material under 2 mm. and contains a small amount of unsegregated particles up to 10 mm. in the largest dimension, the sampling unit is taken by means of a specially designed thief (Fig. 1) or by means of a suitable shovel, dipper, etc.

(*a*) From large shipments, as shipholds, scows, barges, cars, etc. On a line through the center of the holder, lengthwise, take portions with the thief every five feet. Repeat this operation on each of two lines parallel with and half-way between the first line and each side of the holder. Combine all the portions for the gross sample. If the shipment is composed of more than one holder, combine the portions from each holder into a composite gross sample.

(*b*) From tram-cars, carts, buggies, etc.

Take a specified portion from each holder with the thief or shovel and combine all portions for the gross sample.

(*c*) From barrels, bags, wheelbarrows, etc.

Take a portion from every *n*th container and combine the portions for the gross sample.

(*d*) From small piles (not more than six feet in height).

With the thief, take one portion vertically at the peak of the pile and one vertically at each of ten points uniformly distributed along a line around the pile half-way between the peak and the edge of the pile. Combine these portions for the gross sample.

(*e*) From a well-mixed bulk of material (from mixers, packing machines, etc.).

After allowing a specified quantity, according to the condition of the material and type of apparatus, to flow past the sampling point, take the specified quantity for a sample. Periodic samples may be taken in the same manner, as often as desired.

6. **From Wet Material.** — Wet materials arrange themselves in several classes:

(*a*) When the material is thoroughly wet but not dripping, take the sample by any of the foregoing suitable procedures, keeping the collected portions in moisture-tight containers.

(*b*) When water is dripping from the material, take the sample as prescribed for the particular material by one of the foregoing pro-

cedures and allow the total gross sample to drain, the drainage and remainder of the sample being weighed and recorded. If further elimination of water is necessary either by air drying, artificial drying or pressing, before the gross sample is reduced to the laboratory sample, the total water eliminated must be calculated and taken into account in the final evaluation of the material to the original wet condition.

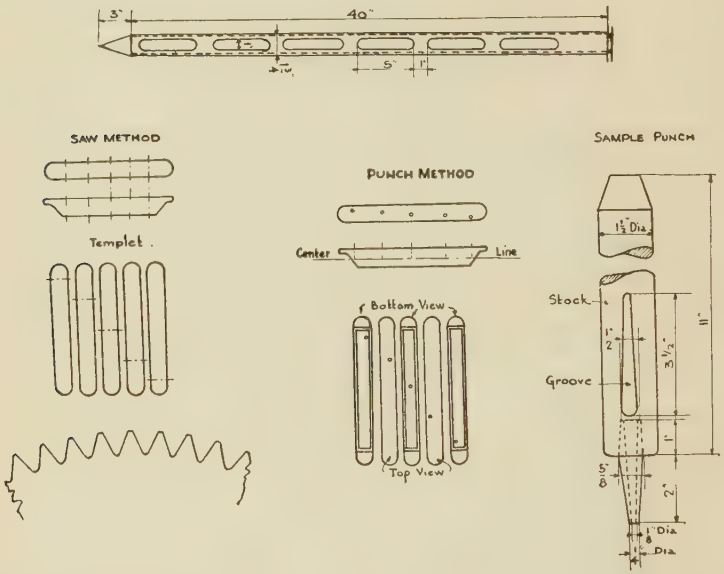



FIG. 1. APPARATUS FOR SAMPLING SOLIDS

Sect. 1. Thief for sampling solids $\frac{1}{4}$" diameter or smaller. Openings to correspond. Both tubes hollow and to be made from $\frac{1}{16}$ sheet brass (hard). Inside tube to fit snugly into outside tube. Point to be steel or iron.

Sect. 1*a*. Saw Method of Sampling Pigs. The bars are sampled in sets of five, according to Templet as shown. Saw is sharpened on Emery Wheel to size and shape here shown.

Sect. 1*b*. Punch Method of Sampling Pigs. The bars selected as samples are placed in a line, with every other bar, bottom side up. The sampling is done according to Templet in sets of five bars each, as indicated above. The punch must be driven through the bar. If a large sample is desired, the bars are turned over and sampled on the other diagonal.

Sect. 1*c*. Sample Punch.

In case this water carries some of the material in solution, it will be necessary to ascertain the amount of this by analysis and include the results in the final evaluation.

(*c*) When fine solid material is non-uniformly suspended in a liquid several vertical sections of the material may be taken by means of a specially designed thief and combined for the gross sample.

7. **From Hygroscopic or Deliquescent Materials.**

(*a*) When such material is contained in airtight containers which may be readily opened and closed, take a sample by means of a thief (Sect. 1), when the material does not contain resistant particles, larger than $\frac{1}{2}$ inch in cross section or, otherwise, by means of a small scoop or shovel. These increments should be placed and retained in an airtight receiver until ready for the analysis.

(*b*) When such material can be sampled while being transferred to the final container for shipment, small and equal increments at uniform and regular intervals are taken directly from the stream by means of a suitable dipper and combined for the gross sample.

8. **From Kilns, Roasters, Dryers, Furnaces, etc.** — This class of material constitutes a special case, and, consequently, the size of sampling unit and manner by which it may be taken will be specified according to the size of particles and character and condition of the material.

9. **Sampling Non-ferrous Metals and Alloys.**

(*a*) **In the Form of Pigs, Billets, Ingots, Rolls, Slabs, etc.** — One pig, etc., should be taken to represent each ton of metal in the lot and each of these should be sampled by one of the following methods after thoroughly cleaning the surface to be sampled.

(1) By sawing completely through the specimen as illustrated by Sect. 1*a*, Fig. 1. The sawdust from all the specimens is then thoroughly mixed and quartered down on a clean surface and the required amount of sample drawn.

(2) By punching or drilling completely through if the equipment permits, or half-way through from two opposite sides as illustrated by Sect. 1*c*, 1*b*, Fig. 1. In this case the holes shall be spaced along a diagonal line from one corner of the specimen to the other. Sampling in this manner may be so arranged that one or more holes are made in each of several specimens of a group in such positions that they represent consecutive positions on the diagonal of a single specimen. (See illustration in Sect. 1*c*.) These punchings or drillings are carefully melted in a clean graphite crucible, and either granulated by carefully pouring into distilled water and thoroughly drying, or by casting into thin slabs which may be sawed completely through in several places and the sawdust treated as described above. Drillings may be chipped and mixed if convenient.

(*b*) **In the Form of Sheets.** — In sampling brass discs, and sheets, when they can be crated so that the edges are flush, recourse can be made to a portable milling machine operated by a $\frac{1}{4}$ H.P. electric motor run transversely across the edges, so adjusted that only a very thin milling is taken from each disc or sheet. These are coned and quartered for the sample. By this method the serviceability of the disc or sheet is not destroyed, and the completeness of the sampling depends only on the accuracy of adjusting the edges in the crate.

### PROCEDURE FOR REDUCING THE GROSS SAMPLE

By combining the several sampling units, the gross sample is obtained which should now be so large that large single chance particles of material could be entirely foreign matter or entirely pure substance and affect only slightly if at all the final sample. Increasing the size of the gross sample increases its accuracy, but cost and convenience of collection and reduction of sample, limit the degree to which this can be carried to advantage. The reduction of the gross sample to the laboratory sample is an operation which must be performed with accuracy and precision. Automatic machinery and labor and time saving devices may be used for this operation adhering closely to the following general scheme with the exception that some materials of uniform comparison need not be finally reduced as small as 6 mm. — 4 mesh — while it may be necessary to finally reduce other material to .14 mm. — 100 mesh — or finer.

In sampling large shipments, the gross sample may become excessively large and unwieldy. This may be obviated by periodically reducing the gross sample by the Standard Long Pile and Alternate Shovel Procedure, and subsequently compositing these reduced portions for the final gross sample.

### IV. Reduction of the Gross Sample

(Approx. 1000 lbs.) crushed to about 22.6 mm. — 1 mesh; thoroughly mixed and halved by the Long Pile and Alternate Shovel procedure.

| | |
|---|---|
| *Discard* | One-half crushed to about 16 mm. — 1.5 mesh; mixed and |
| $\frac{1}{2}$ | halved by the Long Pile and Alternate Shovel procedure. |
| $\frac{1}{2}$ | One-half crushed to about 11.3 mm. — 2 mesh; mixed and halved by the Long Pile and Alternate Shovel procedure. |
| $\frac{1}{2}$ | One-half crushed to about 4 mm. — 5 mesh; mixed by rolling on canvas; halved by Cone and Quartering procedure. |
| $\frac{1}{2}$ | One-half ground to about 2 mm. — 10 mesh; mixed by rolling on canvas; halved by riffling (or sampling machine) or by the quartering procedure. |
| $\frac{1}{2}$ | One-half mixed and riffled down to about 8 lbs. |

The entire eight pounds is then further reduced and the required sample taken according to the character of the particular material.

A portion for the determination of moisture may be taken at some point during the reduction according to the character of the sample and manner in which the moisture test is made. When a moisture sample is wanted it is necessary that the sampling units be collected and stored under conditions whereby moisture would not be lost or absorbed. The mixing, crushing and halving operations, preceding the taking of the sample for moisture should be accomplished as rapidly as possible.

In case the gross sample contains an excessive amount of water which would be lost in the subsequent operations necessary to reduce it to the laboratory sample, it should be kept in a tight container during the collection of the various increments, after which it is weighed and allowed to air-dry, or it may be dried artificially, and re-weighed. It is then in a condition to be reduced to the laboratory sample according to the above scheme, taking into account, of course, the moisture thus driven off from the original gross sample in the final calculation for the evaluation of the material.

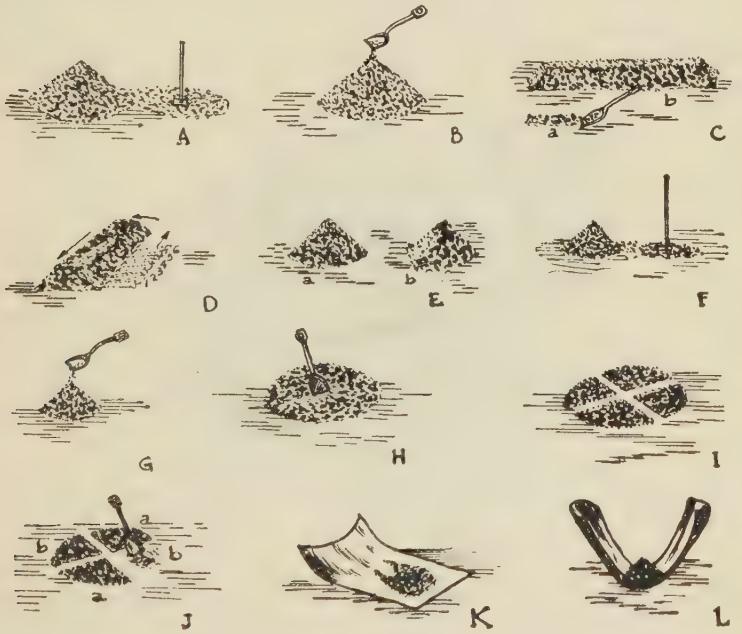



FIG. 2. METHOD OF SAMPLING ORE

**Reduction of Gross Sample (Long Pile and Alternate Shovel).** — This procedure is based upon the method recommended and used by the U.S. Bureau of Mines.

1. Thoroughly mix the entire gross sample, after crushing in a suitable manner until all pieces are approximately one inch or less in any dimension, by shoveling it into a cone-shaped pile, depositing each shovelful on the apex of the pile.

2. Shovel all of the material into a pile about the width of the shovel and approximately 10 feet long according to the total amount of material, spreading each shovelful uniformly over the whole length of the pile, beginning alternately from opposite ends. (Fig. 2, *C*.)

3. Divide the long pile into two equal portions by beginning on one side of the pile, at either end, and take successive shovelfuls, advancing each time by the width of the shovel around the pile, combining the first and every alternate shovelful into a neat cone-shaped pile as in No. 1 and discarding the second and every alternate shovelful (Fig. 2, *D* and *E*).

4. Repeat the above operation on the reserved portion until a portion of about 500 lbs. is obtained.

5. Crush the material until no piece is greater than approximately three-fourths inch in any dimension, and then repeat the above operation (No. 3).

6. Crush the material until no piece is larger than approximately

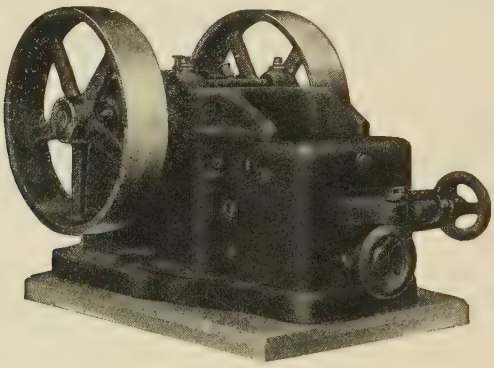


FIG. 3.[1] JAW AND TOGGLE CRUSHER FOR COARSE AND MEDIUM FINE GRINDING

one-half inch in any dimension and then repeat the above operation.

7. A portion of about 125 lbs. is now obtained which is further reduced by the "Cone and Quartering Procedure" (No. 3).

### V. Reduction of Gross Sample (Cone and Quartering)

1. Mix the material amounting to about 125 lbs. by crushing to pass a 4 mm. — 5 mesh — sieve and shoveling into a neat cone (Fig. 3, *F* and *G*).

2. Flatten the cone by pressing the apex vertically down with the shovel or board so that, when quartered, each quarter will contain the material originally contained therein.

3. Divide the flattened pile into equal quarters by passing a straight edge board vertically twice through center of the pile at right angles, each time drawing half of the pile a few inches to one side (Fig. 2, *H* and *I*).

[1] Courtesy of Sturtevant Mill Co.

4. Discard two opposite quarters and brush away all fine particles from the exposed surface (Fig. 2, *J*).

5. Crush the remaining quarters to pass a 2 mm. — 10 mesh — sieve. Mix thoroughly by shoveling into a neat cone.

6. Repeat operations No. 3 and 4 or riffle to about 20 pounds.

7. Grind the retained sample to pass a .85 mm. — 20 mesh — sieve. Mix the material thoroughly on a clean canvas by raising alternate opposite corners of the canvas, thus rolling the material from side to side one hundred times (Fig. 2, *K* and *L*).

8. Treat the sample further as required by the particular material being sampled.

It is, of course, impossible to reduce hygroscopic or deliquescent gross samples to the laboratory sample according to the above scheme

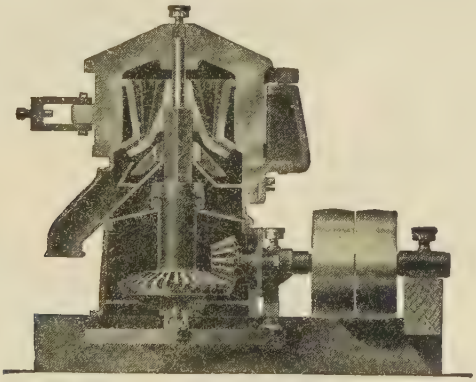


Fig. 4.[1] Crusher and Grinder in Cross Section

unless they can be dried or otherwise transformed into a stable condition. When it is necessary to reduce such material it should be done rapidly and by hand, under the most favorable atmospheric conditions in regard to humidity, etc. When a large sample is taken for analysis the extent of the reduction of the sample will depend upon the size of the sample taken for analysis.

### VI. Apparatus for Reduction and Preparation of the Sample

Any sampling system which does not properly control the ratio of the size of largest particle to the size of sample can not be depended upon to produce a representative sample. The proper ratio for almost all material will be obtained by following the procedure outlined under the heading "Procedure for Reducing the Gross Sample." This reduction process is greatly facilitated by the use of suitable crushers,

[1] By courtesy of Sturtevant Mill Co.

grinders, riffle samplers and mixing devices. The following examples of such apparatus are therefore given as an aid to the designing and equipping of the sampling room, the size and capacity of which will

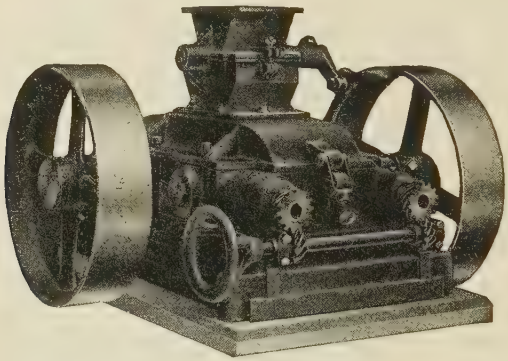


FIG. 5.[1] ROLL GRINDER FOR BRITTLE MATERIAL

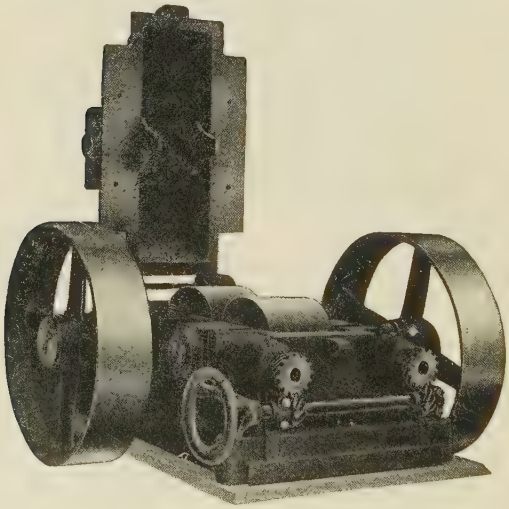


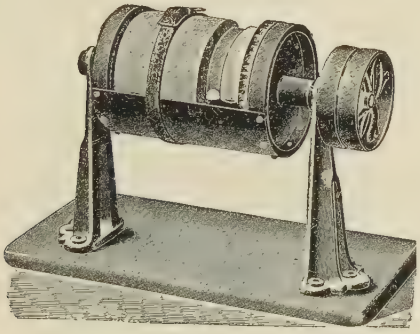
FIG. 6. ROLL GRINDER WITH CASE LIFTED TO SHOW INTERIOR

be determined by the number, character, and size of the gross samples to be handled.

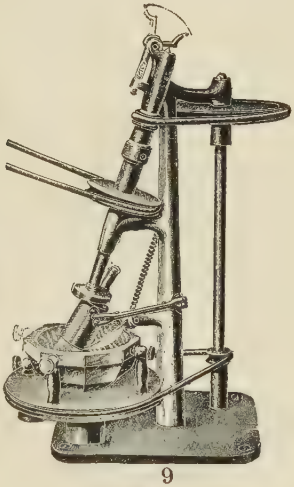
**Crushers.** — A jaw and toggle crusher is shown in Fig. 3. This is

[1] By courtesy of Sturtevant Mill Co.

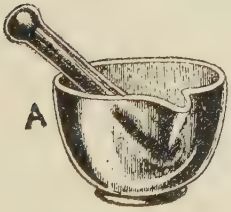
a satisfactory crusher for coarse, medium and fine crushing and permits a considerable range of adaptability to suit varying conditions and requirements. Simple adjustments allow the capacity to be varied from about 200 pounds per hour for the production of fine material to 700 pounds per hour for coarser material when considering only one of the several sizes of this type of crusher. The parts are



7



9



8

10

FIGURES. 7, 8 A AND B, 9 AND 10 SHOW TYPES OF GRINDERS FOR PULVERIZING LABORATORY SAMPLES

readily accessible for cleaning and repairing. By means of this type of crusher it is possible to reduce the material to about 4 mesh.

**Grinders.** — *Grinders* are necessary for reducing the material finer than 4 mesh and may be of the roll, disc or coffee mill type, according to the character of the material.

Roll grinders are especially adapted for brittle material. Figures 5 and 6 illustrate a type of roll grinder which may be readily cleaned

and has a capacity of 100 to 1,000 lbs. per hour when producing a reduction to a fineness of 60 mesh and 2 mesh respectively. Disc grinders have a somewhat greater range of adaptability than the roll grinder and will reduce brittle or tough material to a high degree of fineness. The grinding is accomplished between a stationary and a revolving steel or iron disc, the output being small and fine or large and coarse according to the adjustment.

The coffee mill type of grinder is adaptable to soft or tough materials which have a tendency to stick to the rolls of the roll grinders

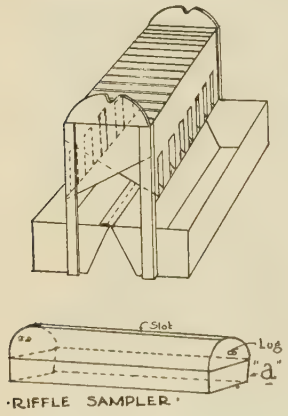



FIG. 11

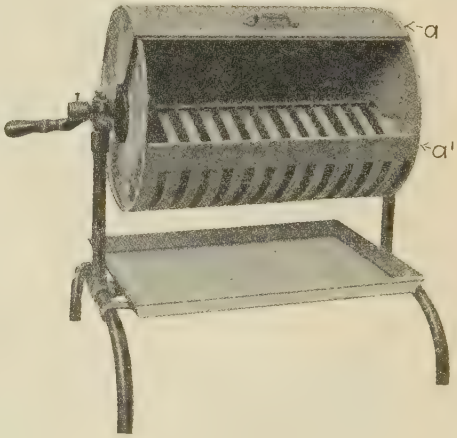



FIG. 12

FIG. 11. Riffle Sampler. "a," cover to fit tightly over one of the boxes with slot in rounded tops — also fitted with two lugs which fit in ends of riffle and help to rock evenly.

FIG. 12. The cut shows the apron of the cylinder of this machine open for receiving the sample. After the sample is poured in, the apron's position is shifted, *a* being moved to *a'*. The cylinder is then revolved counterclockwise. The closed sides of the riffles plow through and thoroughly mix the sample, and no sample can be discharged through the riffle while the cylinder is revolving in this direction if the level of the sample is below the axis of the cylinder. After the sample has been mixed the cylinder is rotated one turn clockwise; the sample in the cylinder is then cut by the planes of the riffle and half of it is discharged into the receiving tray. The sample remaining is again mixed by revolving the cylinder counterclockwise. By alternately changing the direction, the sample is alternately mixed and halved until twice the size of sample required remains in the cylinder. The tray is then emptied of the discarded material, and the sample remaining, mixed and halved, and the sample caught in the tray is bottled and becomes the official sample, while the sample remaining in the cylinder is bottled and held as the reserve sample. The interior of the machine is easy of access and should be brushed clean after each sampling operation.

or to clog the discs of some types of disc grinders. Many kinds of coffee mill type grinders have been developed from which selection can

be made according to the character of material under consideration. Figs. 4 and 5 illustrate very good coffee mill types. When reducing material to extreme fineness the ball mill, special small laboratory grinders, the bucking board and mortar and pestle are always applicable for small samples.

Another type of crusher and grinder which has been developed particularly for sampling coal is shown by Fig. 4. This crusher will reduce the material and deliver an accurate ten per cent sample in one operation. By repeating the operation on the aliquot the sample may be further reduced.

For many materials this crusher would serve to entirely reduce the gross sample to the laboratory sample with a very small amount of labor.

## VII. Mixing and Dividing Samples

Large samples (500 lbs. or more) are usually mixed and divided by the "Long Pile and Alternate Shovel" procedure or (500–100 lbs.) by the "Cone and Quartering" procedure.

Small samples (less than 100 lbs.) are usually mixed by rolling on a clean canvas, whereby the particles are given a rolling motion in alternately opposite directions, the dividing being done by quartering or, more accurately and rapidly, by passing it through some form of a riffle. A convenient and serviceable type of riffle is illustrated by Fig. 11. Another and more simple type is shown by Fig. 12.

## VIII. The Use of Standard Sieves

This section is based upon the specifications issued by the U.S. Bureau of Standards (1912) and adopted by the Amer. Inst. of Mining Engineers (1917).

The essential quantity in the definition of a sieve of a particular size is, primarily, the size of the openings through which the particles to be sifted are to pass.

A series of sieves of different sizes should have the openings vary uniformly, according to the size of the particles desired to separate. Inasmuch as most of the grinding of substances to fine particles is chiefly with the object of increasing the surface upon which some chemical action is to take place, the opening of such a series of sieves should vary in such a way that the square or fourth powers of the width of the openings shall form a geometrical series.

While the sampling process does not require extremely accurate sieves it is advisable to use those which conform approximately to a standard specification. Consequently whenever reference is made to a sieve it will be understood to comply with the following specifications, which have been adopted by a conference of representatives of various scientific and technical societies, government bureaus, and private firms, held at the U.S. Bureau of Standards.

This sieve scale is essentially metric. The sieve having an opening of 1 mm. is the basic one and the sieves above and below this in the series are related to it by using in general the square root of 2 (1.4142), or the fourth root of 2 (1.1892), as the ratio of the width of one opening to the next smaller opening. The first ratio is used for openings between 1 mm. and 128 mm. while the fourth root of 2 is used as the ratio for openings below 1 mm. to give more sieves in that part of the scale.

| Designation of Sieve, Metric System | Customary Usage | Opening | | Number of Mesh per Linear | | Diameter of Wire | |
|---|---|---|---|---|---|---|---|
| | | Mm. | Inch | Centimeter | Inch | Mme | Inch |
| 128.0 mm. | | 128.0 | 5.04 | | | 9.5 | 0.375 |
| 90.5 " | | 90.5 | 3.56 | | | 9.5 | 0.375 |
| 64.0 " | | 64.0 | 2.52 | | | 6.4 | 0.25 |
| 45.3 " | | 45.3 | 1.78 | | | 5.26 | 0.207 |
| 32.0 " | | 32.0 | 1.26 | | | 4.85 | 0.192 |
| 22.6 " | 1 mesh | 22.6 | 0.891 | | | 4.11 | 0.162 |
| 16.0 " | | 16.0 | 0.630 | | | 3.05 | 0.120 |
| 11.3 " | 2 " | 11.3 | 0.445 | | | 2.67 | 0.105 |
| 8.0 " | | 8.0 | 0.315 | 1.0 | 2.54 | 2.00 | 0.079 |
| 5.66 " | | 5.66 | 0.223 | 1.4 | 3.56 | 1.48 | 0.058 |
| 4.00 " | 5 " | 4.00 | 0.157 | 2.0 | 5.10 | 1.00 | 0.039 |
| 2.83 " | | 2.83 | 0.111 | 2.75 | 7.00 | 0.81 | 0.032 |
| 2.00 " | 10 " | 2.00 | 0.079 | 3.9 | 9.9 | 0.56 | 0.022 |
| 1.41 " | | 1.41 | 0.0555 | 5.0 | 12.7 | 0.59 | 0.0232 |
| 1.00 " | | 1.00 | 0.0394 | 7.0 | 17.8 | 0.43 | 0.0169 |
| .85 " | 20 " | 0.85 | 0.0335 | 8.0 | 20.3 | 0.40 | 0.0157 |
| .71 " | | 0.71 | 0.0280 | 9.0 | 22.9 | 0.40 | 0.0157 |
| .59 " | | 0.59 | 0.0232 | 10.0 | 25.4 | 0.41 | 0.0161 |
| .5 " | 30 " | 0.50 | 0.0197 | 12.0 | 30.5 | 0.33 | 0.0130 |
| .42 " | | 0.42 | 0.0165 | 14.0 | 35.6 | 0.29 | 0.0114 |
| .36 " | 40 " | 0.36 | 0.0142 | 16.0 | 40.6 | 0.26 | 0.0102 |
| .29 " | 50 " | 0.29 | 0.0114 | 20.0 | 50.8 | 0.21 | 0.0083 |
| .25 " | 60 " | 0.25 | 0.0098 | 23.0 | 58.4 | 0.185 | 0.0073 |
| .21 " | 70 " | 0.21 | 0.0083 | 27.0 | 68.6 | 0.16 | 0.0063 |
| .17 " | 80 " | 0.17 | 0.0067 | 31.0 | 78.7 | 0.15 | 0.0059 |
| .14 " | 100 " | 0.14 | 0.0055 | 39.0 | 99.1 | 0.116 | 0.0046 |
| .125 " | 120 " | 0.125 | 0.0049 | 47.0 | 119.4 | 0.089 | 0.0035 |
| .105 " | 150 " | 0.105 | 0.0041 | 59.0 | 149.9 | 0.064 | 0.0025 |
| .088 " | 170 " | 0.088 | 0.0035 | 67.0 | 170.2 | 0.061 | 0.0024 |
| .074 " | 200 " | 0.074 | 0.0029 | 79.0 | 200.7 | 0.053 | 0.0021 |
| .062 " | 250 " | 0.062 | 0.0024 | 98.0 | 248.9 | 0.040 | 0.0016 |
| .052 " | 280 " | 0.052 | 0.0021 | 110.0 | 279.4 | 0.039 | 0.0015 |
| .044 " | 325 " | 0.044 | 0.0017 | 127.0 | 323.0 | 0.035 | 0.0014 |

## IX. Containers for Shipment to Laboratory

Samples in which the moisture content is important should always be collected and shipped in moisture-tight containers. A galvanized iron or tin can with a screw top which is sealed with a rubber gasket

and adhesive tape is best adapted to this purpose. Glass fruit-jars sealed with rubber gaskets may be used, but require very careful packing to avoid breakage in transit. Samples in which the moisture content is of no importance need no special protection from loss of moisture.

### X. Drying Ovens for Moisture Determination

Samples may be dried by means of a forced draft of air at a slightly elevated temperature, or by heating at 100–110° C. in a well-ventilated oven until a constant weight is obtained. The former procedure is particularly adapted to material which has a tendency to

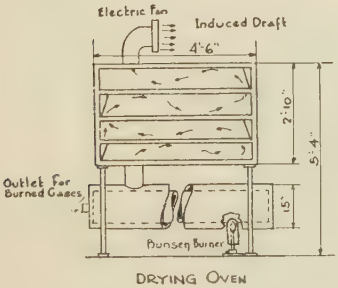



FIG. 13

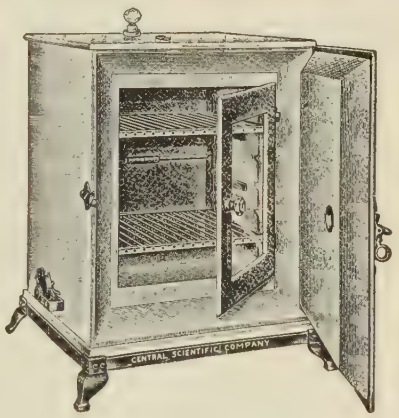



FIG. 14

AIR DRYING OVEN

FIG. 13. Dryer for Coarse Samples. The outlet for air at the top may be connected with a chimney or any other device which will furnish a suitable draft. The sample is spread on tared pans, weighed, and dried at 10° to 15° C. above room temperature, and weighed again. The drying should be continued until the loss in weight is not more than 0.1 per cent per hour.

undergo undesirable chemical or physical changes upon prolonged heating at elevated temperatures or for rapidly removing extraneous moisture preparatory to grinding. The latter procedure is usually employed for quantitative determinations on small finely ground samples. In either case a good system of ventilation and a definite uniform temperature are the chief considerations.

Figure 13 illustrates an oven for drying large samples by means of a current of heated air. Fig. 14 shows a type of oven with a good ventilating system. Fig. 15 illustrates a vacuum drying oven which may be necessary for special work.

This section on sampling was contributed by J. B. Barnitt, Chief Chemist, General Chemical Company. See "Standard Methods of Chemical Analysis," W. W. Scott. Published by D. Van Nostrand Company.

## REFERENCES

"Method of Least Squares Applied to Estimating Errors in Coal Analysis." Technical Paper 171, U.S. Dept. of the Interior.
Bailey, E. G., "Accuracy in Sampling Coal." J. Ind. and Eng. Chem., 1, 161.
Weld, F. C., "Accuracy in Sampling." J. Ind. and Eng. Chem., 2, 426.
Camp, J. M., "The Methods of the U.S. Steel Corporation for the Commercial Sampling and Analysis of Iron Ores." J. Ind. and Eng. Chem., 1, 107. Professional Paper No. 48, U.S. Geol. Survey.
Pope, Geo. S., "Sampling Coal Deliveries." Bull. No. 63 and Technical Paper No. 133, U.S. Bur. of Mines. "The Sampling of Coal," Amer. Soc. for Testing Materials, Standards (1918), 673, 679.
Wolf, A. G., "Sampling of Mine Floors." Eng. and Min. J., 106, pp. 537 and 671.
Daman, "An Automatic Ore Sampler." Eng. and Min. J., 103, p. 188.
Maxwell, "Mill Check on Mine Sampling." Eng. and Min. J., 104, p. 884.
Herr, "Observations on Sampling." Eng. and Min. J., 102, p. 1015.

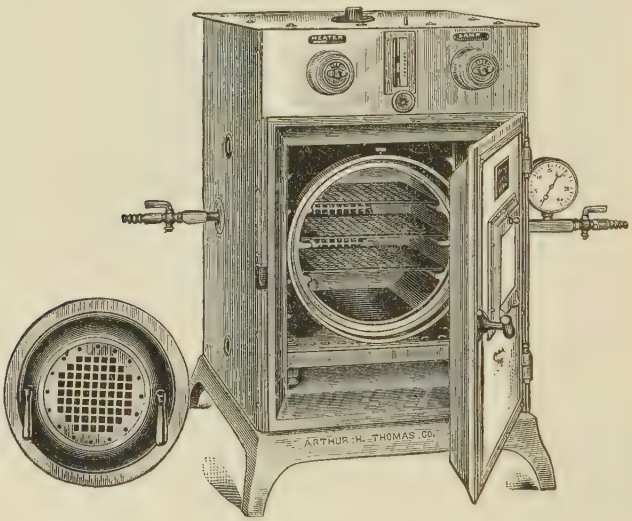



FIG. 15. VACUUM DRYING OVEN

Pearce, "Ore Sampling of a Custom Mill." Eng. and Min. J., 104, p. 66.
"Preparation of Laboratory Samples." J. Ind. and Eng. Chem., 9, p. 100.
Circular No. 39, U.S. Bur. of Standards.
"Standard Screen Scale for Testing Sieves." Bull. Amer. Inst. of Mining Eng., June, 1917.
Kerr, C. H., "Standard Testing Sieves." Trans. Am. Ceram. Soc., 15, p. 375–380.
Hoover, T. J., "Standard Series of Screens for Laboratory Testing." Eng. and Min. J., 90, p. 27.
Fairlie, A. M., "Standard Sieves and Screens." Metal Ind., 12, p. 113.
"Mechanical Preparations of Solids for Chemical Treatment." Eng., Chem. 9, p. 171.
"Standard Methods of Chemical Analysis," by W. W. Scott. D. Van Nostrand Co., Publishers.

## WEIGHING

### § 21. Use of the Balance.[1]

1. **Construction.** — Quantitative processes involve determinations of the relations existing between two masses of matter, but since both masses are determined by means of a beam balance under identical conditions the distinction between mass and weight can be disregarded. The accuracy of such processes must depend in part upon the accuracy with which the two weighings are made, and instrument makers have developed certain forms of balances known as "analytical balances" the use of which makes it possible to reduce the errors from this source to insignificant proportions. The details of the mechanism used by different makers for the adjustment and protection of such balances vary, but since all are based upon the use of essentially the same principles, only one type will be described here.

2. The beam of such a balance is represented in Fig. 16. It is

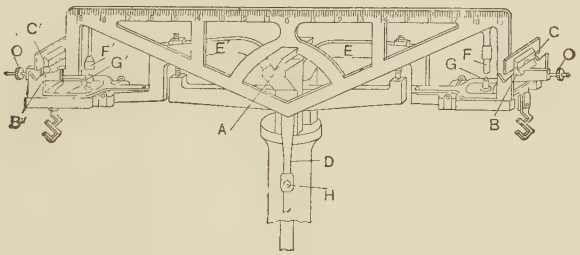



Fig. 16. Beam of an Analytical Balance

constructed of such material, and in such a form, as to combine the maximum degree of rigidity and strength, with the minimum weight. It is suspended at its center on a horizontal axis, which is made of agate and accurately ground to a knife-blade edge, as shown at $A$ of the figure. This axis rests upon a strip of polished agate supported upon the top of a pillar, and the beam is free to turn in a vertical plane about this axis. Two other knife-blade edges $B$ and $B'$, which are of a similar construction but with edges turned upwards instead of downwards, are fixed at the two ends and equidistant from the center. These edges sustain specially constructed stirrups, which are also provided with strips of agate, $C$ and $C'$ of the figure, at the points of contact; from them are suspended two pans, one of which supports the substance being weighed, and the other the weights used. The beam may be regarded as a compound lever in which the fulcrum is at the axis of suspension. If the two arms are of equal length, and if the pans and the loads which they contain are of equal weight,

[1] "Principles of Quantitative Analysis," by W. C. Blasdale. D. Van Nostrand Co., Publishers. By courtesy of the author.

the effect of the force of gravity upon the two ends of the beam is identical, and a depression of one end of the beam will produce a series of vibrations similar to those of a pendulum.

The process of weighing consists in placing the substance whose weight is to be determined in one pan, and adding weights to the other until the two counterbalance each other. This point can be recognized by observing the movements of the beam, and a pointer, the upper part of which is shown at $D$, is attached to it for the purpose of magnifying these movements; a small ivory scale, represented by Fig. 17, is placed just back of the end of the pointer, in order to make it possible to measure and record the magnitude of these movements with respect to the central axis. The center of this scale, which is directly below the axis of suspension, should be marked 10, the tenth division to the left 0, and the tenth to the right 20; this method of marking the scale at once indicates whether the numbers recorded are to the left or the right of the center.

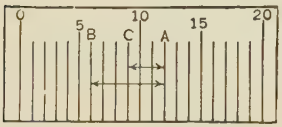


Fig. 17. Scale of Balance

3. As the movement of the beam is greatly retarded by friction, and as the friction losses increase very rapidly as the knife-blade edges lose their sharpness, it is necessary to protect these bearings against needless wear; hence, analytical balances are often provided with two sets of rests, known as "beam-rests" and "pan-rests" respectively. The beam-rests are controlled by a milled button, placed at the center and on a level with the floor of the balance case. When rotated it turns an eccentric, which raises a rod passing through the center of the pillar of the balance, and this in turn raises two hinged arms $E$ and $E'$, which lift the knife-blade edge $A$ from the agate plate, and also the stirrups sustaining the pans from the knife-blade edges $B$ and $B'$ on which they rest. The hinged arms are also provided with two studs $F$ and $F'$, which fit into a cup and a trough terminating the two studs $G$ and $G'$, fastened to the beam. The effect of raising and lowering the beam-rests is to bring the beam into exactly the same position with respect to the agate plate upon which it rests.

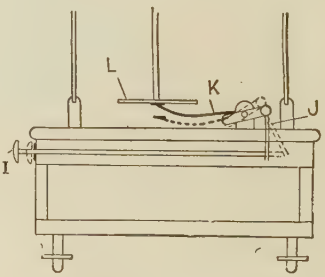


Fig. 18. Base of Balance Case

4. The pan-rests are controlled by a small knob placed at the left of the center, as shown at $I$ of Fig. 18. When a slight pressure is applied to this button, the rod to which it is attached moves the lever $J$ which carries two arms $K$ and $K'$ and causes these to drop. Ordinarily these arms impinge upon the bottom of the pans $L$ and $L'$ and

(K′ and L′ are not shown in the cross section drawing above.)

prevent needless vibration and wear of the bearings $B$ and $B'$, but when they drop the beam is free to vibrate. As a protection against dust, moisture and air currents, the entire apparatus is enclosed in a glass case, one side of which consists of a movable slide of the same material.

### NOTES ON CARE OF THE BALANCE

§ 22. 1. The balance is the most important instrument used in Gravimetric work and upon its accuracy and sensitiveness correct

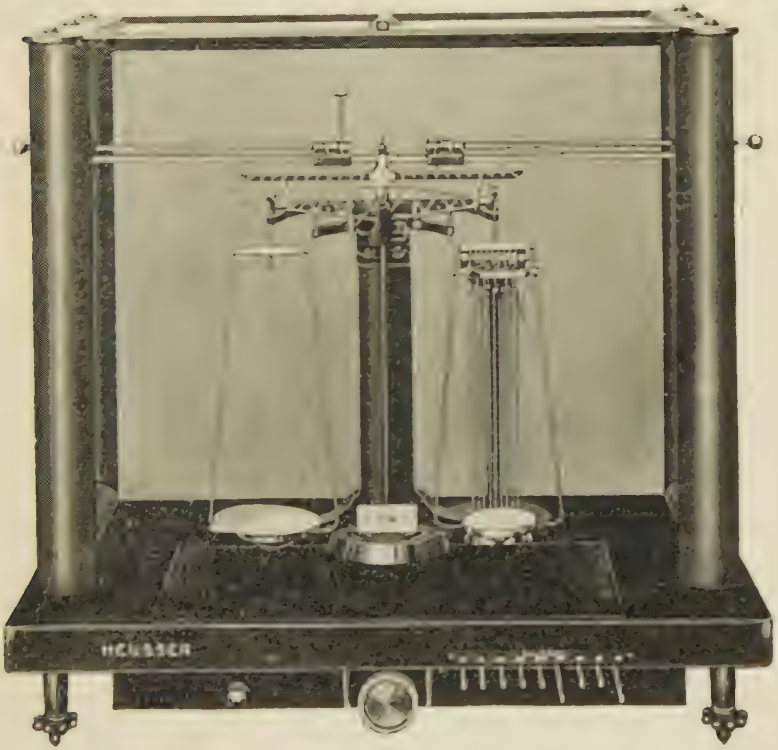


FIG. 19. ANALYTICAL BALANCE[1]

results depend. It is important, therefore, to handle the balance with care, as its adjustments are fine and easily deranged. The agate knife edges should be protected, as far as possible, from jars or undue friction. During the intervals when weights are being changed and when the balance is not in use the beam arrest should be raised and the pan arrests should be in position, to take off the load from the agate

[1] By courtesy of the Mine and Smelter Supply Co.

knife edges. These agate bearings are vital to the delicacy of the balance.

2. The center of gravity of the balance should be slightly below the point of suspension. If it is above the point the beam will be unstable. If it is too far below this point the balance will not be sensitive. Balances are usually equipped with an attachment for regulating the center of gravity; frequently by a weight, attached to the pointer, which may be raised or lowered at will. This adjustment should be made by the instructor.

3. When the balance is not in use the case slide door should be lowered to keep out the dust.

### SUMMARY OF RULES FOR WEIGHING

**§ 23. 1. Adjustment of Zero Point.** — Dust off the pans with a small, camel's-hair brush. See that the balance is level. Now carefully lower the beam- and pan-rests by means of the milled knob at the base of the balance case. Start the beam to swing by gently fanning one of the pans. The pointer should swing back and forth across the graduated scale, at the base of the pillar support, 10–15 divisions. Make note of the points of extreme swings of the pointer, two swings in each direction should be sufficient. The pointer should swing the same number of divisions to the right as it does to the left of the center or 0 point of the scale. Should this mean of the average extreme swings be more than two divisions in error on the scale, it is advisable to adjust the balance.[1] As soon as the zero point has been ascertained raise the beam support when the beam becomes horizontal or nearly so. Always observe this precaution in raising the support.

2. When the balance is adjusted, the beam support being in position, place the object to be weighed at the center of the left pan.

Glass or porcelain apparatus, or solid metallic substances, *if cool*, may be placed directly on the scale pan. All chemicals and all powdered matter should be placed on watch glasses or containers to avoid coming in direct contact with the pans as this may cause corrosion of the pans. Liquids, especially those which are hygroscopic or give off corrosive fumes, should be placed in stoppered weighing bottles and so weighed. The weight of the containers should be ascertained and this weight deducted from the total weight of the container and the product.

3. Before beginning to weigh the object, raise the rider from the beam, if it is resting upon it. Select a weight that you estimate should counterbalance the object and place it on the center of the right pan. Now lower the beam-rest and pan-rests and note the direction of the swing of the pointer. If it swings to the left the weight is too much, if to the right it is not sufficient. Now raise the beam

[1] This should be done by one thoroughly familiar with the operation and construction of balances.

support to steady the pans, (See Fig. 16), remove the weight if too much and replace with another of the next lower denomination, or add a weight as the case demands. Lower the beam support and pan arrests and again note the swing of the balance pointer. Repeat the operation until the object is counterbalanced by weights or is within 10 milligrams of this point. The final adjustment is now made by means of the rider, the balance case door being closed to avoid disturbance of the beam by air currents. By means of the rider it is possible to weigh to $\frac{1}{10}$ of a milligram, the total scale on the beam representing 10 milligrams and each division a tenth. The numerals on the beam represent milligrams.

4. Weights should be moved by means of forceps. They should not be handled by the fingers.

5. The objects placed on the pan should be cool (room temperature or nearly so). Hot objects should never be placed on balance pans. An accurate weight cannot be obtained of the material when it is hot. Always cool in a closed desiccator, to avoid any chances of the material picking up moisture from the air.

6. Be careful not to spill substances on the pans or in the balance case. In case of accident, clean the balance before proceeding. Never leave a balance dirty.

7. **Checking the Weight.** — Make note of the weights removed from the weight box by recording these from the empty spaces in the box. Now replace the weights in the box starting with the largest weight on the pan and ending with the lightest. Does this tally with the first weight recorded? Record the weight indicated by the rider.

Fig. 19A.

8. Before leaving the balance attend to the following —

(*a*) See that both the beam and the pan supports are supporting the beam and pans.

(*b*) Raise the rider from the beam.

(*c*) Brush out the case if any material has been spilled in this.

(*d*) Shut the door of the balance case.

(*e*) Take care of the box of weights.

## SOLUTION

**§ 24. Apparatus used for Decomposition of the Sample.**

1. **Beaker.** — This is the most commonly used vessel in which decompositions are made. It is especially useful in laboratories where a large number of determinations are made at one time. For general work the author prefers a beaker of the deep Griffin form of about 250 cc. capacity. During the treatment the vessel is covered by a clock glass which extends slightly beyond the edge of the beaker. When evaporations are conducted the clock glass is raised on glass riders, V-shaped glass rods two inches in length, which rest on the rim of the vessel. This permits the escape of steam and lessens condensation. Fig. 20.

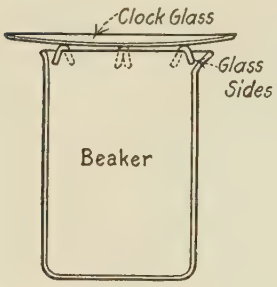



FIG. 20

2. **Erlenmeyer Flask.** — This vessel is useful in decompositions and is commonly employed where spattering is apt to occur. A funnel, whose stem has been cut off, prevents loss through the neck of the flask but permits the escape of steam. Fig. 21.

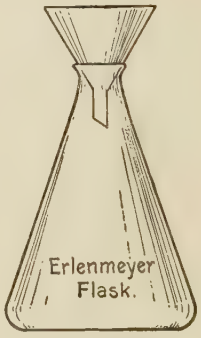



FIG. 21

In evaporations with either type of vessel it is advisable to conduct the last stage of evaporation at a comparatively low heat, on a steam bath, or by placing an asbestos mat between the vessel and the hot plate, otherwise spattering is apt to occur.

The beaker is more easily washed out and any adhering material on the sides may be readily removed by a rubber-tipped glass rod "policeman" which should be used in "copping out" the vessel.

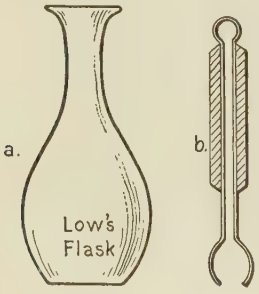



FIG. 22

3. **Low's Flask.** — The "copper flask" type of flask is shown in Fig. 22*a*. It has an advantage over the Erlenmeyer flask as it may be held more easily and manipulated directly over a free flame. A. H. Low uses this form of decomposition vessel almost entirely for general work with ores, even conducting bisulphate fusions in the flask. Where individual determinations are made the decomposition may be effected very rapidly and the excess of reagent expelled in three or four minutes, where with the beaker or Erlenmeyer half an hour would be required.

The flask is held by tongs — Fig. 22*b*. Wood covers the portion held by the hand. During the treatment and the evaporations the flask is kept in constant motion. This prevents bumping and facilitates decomposition by keeping the material constantly agitated. In making fusions the flask is moved slowly over the flame. When cooling the fusion a rotary motion is given the flask so as to spread the melt evenly over the wall. This prevents the vessel from breaking and at the same time makes a subsequent solution of the melt easily accomplished. A flask of 300 cc. capacity is best for general work.

4. **Casserole.** — The porcelain casserole with handle, Fig. 23, is useful in conducting evaporations on the steam bath or hot plate of large amounts of liquid. The casserole should be covered by a clock glass raised on riders, during evaporations.

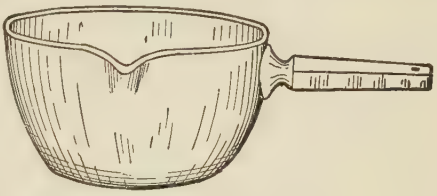


Fig. 23. Casserole

§ **25.** 1. **Fusions.** — The insoluble residue remaining from an acid treatment of a substance may be brought into solution, generally, by fusion with an appropriate flux. The fusions are made in crucibles (20 cc. capacity) of silica, iron, nickel, silver, " palau " (gold-palladium 80 : 20) or platinum. Potassium bisulphate fusions may be made in silica or glass as well as in platinum; sodium carbonate fusions may be made in iron, nickel, " palau," and platinum; hydroxide or peroxide fusions may be made in iron, nickel or silver crucibles; sodium carbonate potassium nitrate fusions may be made in platinum, but hydrochloric acid should not be used in dissolving the fusion as the chlorine liberated will attack the platinum. See § 34, II on the care of platinum.

2. In making fusions the sample is well mixed with six to ten times its weight of the fusion mixture and is placed over a thin layer of the flux in the crucible and then covered by a lid of the same material as that of the crucible. Heat is applied cautiously until the mixture melts, the heat being raised during the action. When the melt has reached a quiet fusion and the resulting molten mass has become clear and homogeneous, the action is complete. One of several methods is now employed to facilitate the subsequent solution of the material.

(*a*) A stiff platinum rod is placed in the molten mass and held in place until this has cooled sufficiently to solidify around the wire. By reheating the crucible the mass of fusion may be lifted out, cooled and together with the crucible placed in the beaker in which the subsequent treatment is made.

(*b*) The molten mass may be poured into a crucible lid of sufficient capacity and when cooled placed in the beaker together with the crucible.

(*c*) The molten mass is cooled by rotating the crucible in such a way

that it solidifies in a layer on the sides of the crucible. The crucible is placed on its side in the beaker.

3. If the melt is allowed to cool in a mass, its subsequent solution is difficult, requiring considerable time.

4. Water is now added to the material and the mixture heated until the mass disintegrates. The beaker is covered by a clock glass and the additional solvent now added. This may be hydrochloric or sulphuric acids, ammonium carbonate or any other appropriate solvent. The liquid may be poured through the lip of the beaker without uncovering. This avoids loss due to effervescence.

Details of the special procedures are given throughout the work.

**§ 26. Amount of Sample.** — The quantity of the sample required depends largely upon the substance and the amount of constituent sought in the sample. In case of ores, where the principal constituent is desired, for example lead in galena, iron in magnetite, alumina in bauxite or sulphur in pyrite, a comparatively small sample is sufficient, namely 0.5 to 1 gram of the ore. On the other hand if the constituent sought is present in small percentage down to mere traces, 5, 10 or as much as 100 grams of the sample may be taken. Fortunately colorimetric processes enable us to determine many of the substances in extremely minute amounts so that one-gram samples are generally sufficient for most analyses. In the volumetric determination of constituents in steel, 1–5 grams are generally taken. 0.5 to 1 gram of alloys is generally taken for their analysis.

**§ 27. Decomposition of the Material.** — In the instructions for the solution of the material special procedures are often given owing to the predominance of some particular compound or compounds present. Directions are given for example for oxides, others for sulphides, and again others for silicates, etc. The chemist is frequently at loss to know what procedure to select as the mere inspection of the material frequently will furnish him no information as to its predominating trait. In the following paragraphs we will attempt to give a few examples of substances that are abundant in nature or that may be commonly received for analysis in a technical laboratory. Commercial products such as inorganic synthetic compounds, acids, salts, bases, need not be considered here.

## MINERALS AND ORES

### I. Carbonates

These occur very extensively in nature. Carbonates treated with acids (such as HCl, $H_2SO_4$) effervesce and give off carbon dioxide, either in the cold or upon heating. See chapter on carbon. Carbonates give off carbon dioxide when highly heated and oxides of the elements are formed.

**Typical examples of carbonates.** — (*a*) *Calcite,* $CaCO_3$, is a colorless or white, frequently transparent (easily scratched with a knife) substance with vitreous lustre. White in powdered form. Readily decomposed by heating with hydrochloric acid.

(*b*) *Dolomite,* $CaCO_3.MgCO_3$, has a vitreous or pearly lustre in lumps, seldom transparent, usually white, or yellowish in well developed crystals. It is slightly harder than calcite. It is soluble in inorganic acids.

(*c*) *Magnesite,* $MgCO_3$, has a vitreous to dull lustre. The mineral is usually white. It dissolves in mineral acids.

(*d*) *Strontianite,* $SrCO_3$, has a vitreous lustre and is usually white or colorless, but sometimes it is green or yellow. Soluble in acids.

(*e*) *Witherite,* $BaCO_3$, has a vitreous lustre and is a white or grayish white mineral. Soluble in hydrochloric acid. Sulphuric acid would form the difficultly soluble $BaSO_4$, which would require fusion with sodium carbonate, if formed, in order to get it into solution.

Carbonates are treated by heating with hydrochloric acid until action ceases and then by addition of nitric acid and further heating. Nitric acid is frequently omitted when its presence is objectionable or unnecessary.

### II. Oxides

These are conveniently classified as A, Oxides of silicon; B, Oxides of the Semi-Metals; C, Oxides of the Metals.

*Typical examples.*

A. **Quartz.** — This is a very common mineral in nature. It is an essential constituent of granites, sandstones, quartzites. The color is variable: white or colorless, violet, rose-red, brown or black. The lustre is vitreous. The crystals may be transparent, translucent or opaque. Silica, $SiO_2$ is practically insoluble in mineral acids with the exception of hydrofluoric acid, which decomposes it with the formation of the volatile (poisonous) silicon tetrafluoride, $SiF_4$. In presence of water, which is invariably the case, fluosilicic acid, $H_2SiF_6$ is formed.

B. **Oxides of the Semi-Metals.** — *Typical examples.* (*a*) Arsenolite, $As_2O_3$, is a colorless or white, earthy compound. Soluble in alkalies.

(*b*) *Senarmonite*, $Sb_2O_3$, is a colorless gray mineral, occurring with antimony ores. Soluble in alkalies, hydrochloric and sulphuric acids.

(*c*) *Bismite*, $Bi_2O_3$, is an earthy substance, straw yellow, or silvery white pearly scales. Soluble in hydrochloric and sulphuric acids.

(*d*) *Tellurite*, $TeO_2$, soluble in acids and in potassium hydroxide. The oxide is found in form of slender, white to yellow crystals.

(*e*) *Molybdite*, $MoO_3$, straw yellow, tufted forms and earthy. Molybdic ochre is a hydrous ferric molybdate, $Fe_2O_3.3MoO_3.7H_2O$. Soluble in hydrochloric, sulphuric acids, and by alkali fusion.

(*f*) *Tungstite*, $WO_3$, yellow or yellowish green, earthy, pulverulent mineral, is practically insoluble in acids, but soluble in alkalies.

C. **Oxides of the Metals.** — In this class are (*A*) Protoxides, $R_2O$ and RO; (*B*) Sesquioxides, $R_2O_3$; (*C*) Intermediate oxides, $R.R_2O_4$; (*D*) Dioxides, $RO_2$.

*Typical examples.*

A. (*a*) *Cuprite*, $Cu_2O$, a mineral of various shades of red with adamantine or submetallic lustre. Soluble in acids.

(*b*) *Zincite*, ZnO, deep red to orange-yellow, translucent to subtranslucent, with subadamantine lustre. Soluble in acids.

B. (*a*) *Corundum*, $Al_2O_3$, a mineral occurring in limestone, dolomite, granite, gneiss, and other crystalline rocks. The precious stones, the red *ruby*, the blue *sapphire*, the yellow *topaz*, the green *emerald*, the purple *amethyst*, are aluminum oxides; *Corundum*, varying from light blue, gray, brown to black; and *Emery*, the impure oxide containing magnetite or hematite, are more common oxides. All of these are practically insoluble in acids, requiring fusion with sodium hydroxide or carbonate to effect solution.

(*b*) *Hematite*, $Fe_2O_3$, red, is a mineral widely distributed in nature. Soluble in hydrochloric and sulphuric acids.

(*c*) *Ilemnite*, $FeO.TiO_2$, resembles hematite, but has a nearly black streak; hematite gives a red streak. Difficultly soluble in acids.

C. (*a*) *Magnetite*, $FeO.Fe_2O_3$, is an iron-black mineral of metallic and splendent to sub-metallic and rather dull lustre. Soluble in sulphuric acid. Addition of stannous chloride to hydrochloric acid assists its solution in this acid.

(*b*) *Chromite*, $FeO.Cr_2O_3$, a dark brown to iron-black mineral with metallic lustre, generally requires an alkali fusion to be decomposed.

D. (*a*) *Cassiterite*, $SnO_2$, white or colorless, but more often brown or black, red or yellow. Powdered, pale brown. Lustre adamantine. Practically insoluble in acids. Requires fusion with sodium hydroxide to effect decomposition. Reduced to metallic tin by fusion with potassium cyanide, or sodium carbonate and charcoal.

(*b*) *Rutile*, $TiO_2$, yellow, red or black mineral with metallic lustre. Solution is effected by fusion with potassium bisulphate, followed by heating the fused mass with hydrochloric acid.

E. *Bauxite*, hydrated alumina, $Al_2O_3.3H_2O$. This is a principal source of aluminum. The mineral is amorphous and earthy and frequently shows concretionary structure. Color variable, according to the amount of iron present, gray, yellowish white to brownish red. Impurities $Fe_2O_3$, $SiO_2$, $TiO_2$, with varying amounts of water. Soluble in sulphuric acid, followed by fusion.

F. *Cinders.* Oxides of iron, alumina, etc. Ignited oxides of iron and alumina are very difficultly soluble in acids, frequently requiring fusion with an acid flux, such as potassium bisulphate, to effect decomposition. Oxides of iron are brought into solution by addition of 4–5 cc. stannous chloride 25% to 20–30 cc. of hydrochloric acid per gram of sample.

G. *Summary of oxides.* It is evident that no set rule will apply to solution of oxides. It is advisable to start with hydrochloric acid and digest until the action ceases, then to add nitric acid and digest. If a residue remains, dilute with water and filter. Fuse the residue with potassium bisulphate. If the residue is due largely to silicates a sodium carbonate fusion should be made. This will also attack some of the difficultly soluble oxides such as tungsten, titanium, chromium.

## III. Silicates [1]

1. In the chapter on silica a list of silicates is given — those soluble in acids and those insoluble. If a silicate is treated with acid and evaporated to dryness, silica, $SiO_2$ is liberated, which is practically insoluble in acids, but dissolves in alkalies. Silicates may be decomposed by fusion with alkalies, the sodium salts being soluble in water. Addition of acid and evaporation to dryness will displace the silica from its combination with the alkali again liberating silica, $SiO_2$.

2. Silica assumes many forms, most of which are crystalline — rock crystal, quartz, sand grains, silts, chalcedony, opal, etc. Asbestos, beryl, clays, feldspars, garnet, kaolin, meerschaum, talc, are silicates. For those desiring further information on the subject of silicates reference is made to the standard works by Dana, Crook, Moses and Parsons, Butler.[1]

## IV. Sulphides

1. Directions in procedures for decomposition of ores are frequently given for treatment of sulphides, the treatment varying according to the constituent to be determined. Usually an oxidizing agent along with hydrochloric acid is called for. This is specially necessary if the determination of sulphur is to be made, otherwise

[1] N.B. "Economic Mineralogy," by T. Crook, Longmans, Green and Co. "Elements of Mineralogy, Crystallography and Blowpipe Analysis," by A. J. Moses and C. L. Parsons, D. Van Nostrand Co. "Dana's Text Book of Mineralogy," revised by W. E. Ford, J. Wiley and Sons. "A Pocket Handbook of Minerals," by G. M. Butler, J. Wiley and Sons.

sulphur is lost by volatilization or by the formation of globules of free sulphur, which are practically inert to reagents commonly used. Oxidizing agents such as potassium chlorate, free bromine in conjunction with nitric and hydrochloric acid are required. (See chapter on sulphur.) On the other hand, if sulphur is not desired it is occasionally advantageous to omit the oxidizing agent. For example, in the determination of lead in galena, PbS, it is advisable to begin with hydrochloric acid alone and expel the sulphur as $H_2S$, before adding nitric acid, otherwise the difficultly soluble lead sulphate would form.

2. Ores containing sulphides are frequently characterized by the glistening yellow particles of metallic lustre that can be seen. These sulphides being heavy may be concentrated by panning much as is gold. A sulphide ore warmed with hydrochloric or sulphuric acid (the test may be made conveniently in a test tube) will give off hydrogen sulphide gas, which has a characteristic odor. The gas will turn moist lead acetate paper black. Sufficient moisture is generally present in the gas so that dry test paper may be used.

Dana[1] classifies Sulphides, Selenides, Tellurides, Arsenides and Antimonides into two subgroups according to the character of the positive element — semi-metal or metal.

3. **Typical examples.** *Realgar*, AsS, aurora-red or orange-yellow mineral, transparent or translucent with resinous lustre.

(*a*) *Orpiment*, $As_2S_3$ has a fine yellow color and pearly lustre.

(*b*) *Stibnite*, $Sb_2S_3$, a mineral with metallic lustre, lead gray to steel gray, sometimes iridescent or blackish, due to tarnish.

(*c*) *Bismuthinite*, $Bi_2S_3$, lead gray color, inclining to tin white, with yellowish or iridescent tarnish and a metallic lustre.

(*d*) *Molybdenite*, $MoS_2$, lead gray color, opaque, metallic lustre.

(*e*) *Galena*, PbS, one of the most widely distributed of the metallic sulphides. The mineral often contains the sulphides of silver, and occasionally that of antimony, bismuth, copper, cadmium, selenium, zinc. Sometimes native silver and gold. The mineral has a pure-lead gray color with metallic lustre.

(*f*) *Argentite*, $Ag_2S$, a blackish lead-gray mineral with metallic lustre.

(*g*) *Chalcocite*, $Cu_2S$, blackish lead-gray color, often tarnished blue or green, dull, opaque, metallic lustre.

(*h*) *Sphalerite* (zinc blende), ZnS. Color commonly yellow, brown, black, also red, green to white, when pure nearly colorless. Transparent to translucent. Resinous to adamantine lustre.

(*i*) *Cinnabar*, HgS, color cochineal red to brownish red to lead gray. Scarlet streak. Adamantine lustre inclining to metallic when dark colored.

(*j*) *Greenockite*, CdS, a nearly transparent mineral with adamantine lustre with citron or orange-yellow color.

[1] "A Text Book of Mineralogy," by E. S. Dana. Revised by W. E. Ford, 1922. John Wiley and Sons.

(*k*) *Millerite*, NiS, brass-yellow to bronze-yellow color, often with gray iridescent tarnish; greenish black streak; metallic lustre.

(*l*) *Pyrrhotite*, composition varying from $Fe_5S_6$ to $Fe_{16}S_{17}$. Frequently contains nickel. The mineral has a metallic lustre. Color between bronze-yellow and copper-red. Tarnishes easily.

(*m*) *Pyrite*, $FeS_2$, lustre is metallic, splendent to glistening. Color a pale brass-yellow. Appearance of gold, hence its name, "Fool's gold." The streak is greenish or brownish black. Opaque.

(*n*) *Arsenopyrite*, $FeS_2.FeAs_2$, a mineral with metallic lustre, silver-white, inclining to steel gray color, giving a dark grayish black streak.

4. A large number of other minerals containing sulphur are commonly found in nature. These are generally decomposed by acid treatment in presence of an oxidizing agent, nitric-hydrochloric acids, hydrochloric acid and bromine, hydrochloric acid and potassium chlorate, etc.

### V. Sulphates

The following are typical examples of the sulphates found in nature. *Potash alum* occurs in kalinite, a colorless, transparent compound, generally colored by impurities. Water soluble.

(*a*) *Barite*, $BaSO_4$, colorless or white, frequently yellow, brown, or red, and crystals sometimes blue. Vitreous or pearly lustre. Solution is effected by fusion with sodium carbonate, extraction of the sodium sulphate with water, and then solution of the barium carbonate residue with hydrochloric acid. Barium chloride is now in solution with the other soluble chlorides.

(*b*) *Celestite*, $SrSO_4$, is a colorless, white or sometimes pale blue mineral, with vitreous lustre. It is decomposed in the same manner as is barite.

(*c*) *Gypsum*, $CaSO_4.2H_2O$, is a colorless or whitish mineral with vitreous lustre; it is found widely distributed in stratified rocks, in clays and in shales. The mineral may be decomposed by hydrochloric acid with addition of a little nitric acid.

### VI. Native Elements

(*a*) *Graphite*, free carbon. Metallic lustre, black shining flakes. Opaque. Insoluble in the common reagents. Burns to $CO_2$ gas in presence of oxygen. It is best determined quantitatively by combustion.

(*b*) *Copper*, Cu, the metal has a characteristic red color (copper-red) and a metallic lustre. The surface is frequently tarnished and coated with malachite, $CuCO_3.Cu(OH)_2$, green, and by other alteration products. It decomposes readily in nitric acid.

(*c*) *Gold*, Au. The metal has its own characteristic yellow color with metallic lustre. The color is paler when silver is present with

the gold, as is generally the case. When the amount of silver exceeds 20 per cent the color is very pale, and the alloy is called " electrum." The element is insoluble in either hydrochloric or nitric acid, but dissolves in a mixture of the two " aqua regia " (2 : 1).

(*d*) *Iron*, Fe. Metallic iron occurs in meteors and in particles or large masses in basalt. The readiness with which the metal combines with acid radicals makes its occurrence in free state a rarity. The metal dissolves in mineral acids.

(*e*) *Mercury*, Hg. The element is found occasionally in the free state with its mineral cinnabar, HgS. It is the only element that is found free in a liquid state, " quick silver." It has a bright metallic silvery lustre. Easily recognized. It dissolves in nitric acid.

(*f*) *Platinum*, Pt. Native platinum is found in rounded or irregular grains in placer deposits and alluvial material. It has a bright silvery metallic lustre. It resists the ordinary reagents of the laboratory, hydrochloric, nitric, sulphuric, and hydrofluoric acids, bicarbonate, carbonate, bisulphate fusions, but is attacked by aqua regia, nitrates with hydrochloric acid, sodium hydroxide, potassium hydroxide, and sodium peroxide fusions. (See Care of Platinum.)

(*g*) *Silver*, Ag. The metal occurs native in veins traversing schist, gneiss, porphyry and other rocks. It occurs alloyed with gold, copper, lead, platinum. The metal is soluble in nitric acid.

(*h*) *Sulphur*, S. Native sulphur occurs in large deposits commonly in volcanic districts. Immense deposits have been found in Louisiana and Texas, and in Sicily, Vanua Lava in New Hebrides.[1]

Sulphur is a yellow element with resinous lustre. Its crystals are transparent. Sulphur may be converted to sulphuric acid by strong oxidizing agents, hydrochloric acid-nitric acid with bromine, or by fusion with sodium peroxide.

### VII. Alloys

These are generally decomposed by treating with nitric acid. Alloys containing elements whose oxides are insoluble in acids are generally treated first with hydrochloric acid, followed by nitric acid. Methods for special treatment will be found in the text where the alloys are discussed.

### VIII. Steel

Steel is usually dissolved in nitric acid or a mixture of nitric hydrochloric, or nitric sulphuric acids.

### § 28. General Rules for Decomposition of Substances.

In general ores should be finely ground. Apparatus for accomplishing this is shown in pages 28 to 31 inclusive.

[1] A mountain of sulphur 1,600 feet high, 100 square miles. Literary Digest, Feb. 4, 1922.

Owing to the variables in ores and alloys it is not possible to have any set procedure applicable to all conditions. It is often necessary to combine two or more methods to effect solution of certain refractory ores. Acid extractions are frequently followed by fusion methods for the solution of the acid insoluble material, likewise fusions require subsequent water extraction followed by acids. The following general rules, however, will be of value.

| *Reagent to Effect Solution* | *Materials* |
|---|---|
| **I. Water** will dissolve | the alkali salts, ammonium, lithium, potassium and sodium acetates, bromides, chlorates, chlorides, iodides, nitrates, nitrites, sulphates. Also arsenates, arsenites, borates, carbonates, oxalates, phosphates, and tartrates. The halides of silver, mercury, and lead are insoluble in water. The arsenates, arsenites, borates, carbonates, oxalates, phosphates and tartrates of the heavy metals require acid treatment to effect solution. Sulphates of Ba, Sr, Ca, Hg″, Pb are insoluble in water. |

**II. Acids**

1. *Hydrochloric acid* decomposes carbonate and oxide ores of B, Ca, Fe, Mn, Mg, P, Sn (reducing agt.), Ti, U, Zn ($SnCl_2$ assists Fe sol.).
2. *Hydrochloric acid* together with or followed by an *oxidizing reagent*, i.e. $HNO_3$, $KClO_3$ etc. Alloys of Al, Sb, Bi, Cu; Cr, Co and Ni steels, ferro silicon, Ti and V steels, sulphide ores of Cu, Ce, Pb, Mo, U, Zn.
3. *Nitric acid*, dilute or concentrated. Alloys of Bi, Cd, Co, Cu, Pb, Mn, silico manganese, ferro manganese, P and Ti steels, ores of Cd, Cu, Mo, Co and Ni.
4. *Aqua Regia.* The metals and alloys of Au, Ir, Hg, V, Pt. Ores of Cd, Hg, Rh, W.
5. *Sulphuric acid.* Ores of Al, Gl, Mn, Pb, Th, Ti, U.
6. *Sulphuric acid* with HF, silicates, Cu ores and alloys.
7. *Hydrofluoric acid*, usually in conjunction with $H_2SO_4$, HCl or $HNO_3$ useful for dissolving ores containing silicates where $SiO_2$ is not to be determined.
8. *KBr, Br, $HNO_3$, HCl* combinations to dissolve pyrites of Pb, Ni, Fe, As, etc. Reactions 1–8 (excepting 7) may be made in glass; 7 in platinum.

**III. Fusions**

1. *Sodium carbonate.* Decomposes silicates of Al, Ca, Ce, Cr, etc.; halides of Ag; sulphates of Ba, Pb.

LIBRARY
9266

2. *Sodium and potassium carbonates.* Silicates of Al, F, Fe, Ni, Se, Te, etc. The mixture fuses at a lower temperature than carbonate alone.
3. *Sodium carbonate with oxidizing agent,* i.e. $KClO_3$, $KNO_3$, $Na_2O_2$, ZnO, MgO. Ores of Sb, As, Cr, Fe, Mo, V, Zr, sulphides, pyrites, etc.
4. *Sodium peroxide.* Ores of Sb, As, Cr, Mo, Ni, V, U, Sn. Certain alloys and steel for chromium, etc.
5. *Potassium acid sulphate* (with $H_2SO_4$). Ores of Al, Sb, Cu, Cr, Co, Fe, Mn, Ni, Rh, Ta, Ti, W. Steel with Cr, Mo, V and W, Th, phosphates, slags.
6. *NaOH, KOH,* basic flux (with or without KF). Oxidized Sb ore, ores of Cr, Sn, Zn, Zr. Sulphides and sulphates in sulphur determinations.
7. Other reagents. *$NH_4Cl$* and *$CaCO_3$* — alkali silicates, *KCN* — tin oxide ore, *CaO*, *$Na_2O_2$*. Organic compounds for halide determination.

Reactions 1, 2, 3, may be carried out in iron, nickel or platinum crucibles, 5 in silica (*porcelain*) or platinum, 4, 6, and 7 in iron, nickel and silver.

§ **29.** The following résumé by W. J. Crook, of reagents used in decomposition of products, is valuable for reference.[1]

**Reagents.** — *Ammonium acetate,* $NH_4C_2H_3O_2$, is a very effective solvent of lead salts, especially the sulphate. It is prepared by adding strong acetic acid to strong ammonium hydroxide until the solution is just acid.

*Ammonium hydroxide,* $NH_4OH$, is a powerful solvent of chloride and bromide of silver.

*Ammonium sulphide,* $(NH_4)_2S$, readily dissolves the sulphides of arsenic, antimony, and tin. This reagent decomposes slowly, losing $NH_3$ and forming $(NH_4)_2S_2$. It should be kept in a dark cool place. To prepare the solution pass a rapid current of pure hydrogen sulphide through a solution of ammonia in a reagent bottle.

*Hydrochloric acid,* HCl, is a powerful solvent and when mixed with $HNO_3$ in the proportion (2–HCl: 1–$HNO_3$) it will dissolve gold and platinum due to the chlorine which is thus liberated in the nascent state.

*Hydrofluoric acid,* HFl, is used to decompose silicates, the silica being volatilized.

*Nitric acid,* $HNO_3$, is a powerful solvent and oxidizing agent. The fuming variety is a more active oxidizer and desulphurizer.

*Sulphuric acid,* $H_2SO_4$, is a powerful solvent and is generally used in a dilute form made by mixing concentrated acid (1.84 sp. gr.) with water in the proportion 1–$H_2SO_4$: $5H_2O$.

[1] Chemical. Lefax, Philadelphia, November, 1918.

*Argol,* $KHC_4H_4O_6$, potassium acid tartrate commercial grade, is a powerful reducing agent and also a basic flux.

*Borax,* cryst., $Na_2B_4O_7.10H_2O$, is an acid flux sometimes used as a cover in place of NaCl. To dehydrate, fuse it in an iron or chalk lined clay crucible, pour the fused mass on a clean surface and pulverize when cold. Melting point, Borax glass, 742° C.

*Charcoal* is a reducing agent and desulphurizer.

*Iron,* metallic, a basic flux, and desulphurizer. Nails or wire about $\frac{1}{8}$ inch dia. generally used. Melting point above 1500° C.

*Lead,* metallic, a basic flux. It is also used as a collector of the precious metals in the assay of gold and silver ores. Granulated lead is used in scorification assays and sheet lead in bullion assays. Its silver content should be determined. Melting point, 327° C.

*Lead flux:* 16 parts sodium bicarbonate, 16 parts potassium carbonate, 8 parts flour and 4 parts borax glass. This mixture serves as a flux, reducing agent, and desulphurizing agent.

*Litharge,* PbO, is a basic flux and an oxidizing and desulphurizing agent. Its silver content should be determined. Melting point, 884° C.

*Silica,* $SiO_2$, is an acid flux. Powdered lime-glass can be used as a substitute. Melting point, $SiO_2$, 1775° C.

*Potassium bisulphate,* $KHSO_4$, is a decomposing agent and an acid flux. Silica is not made soluble by this reagent. Melting point, 200° C., $K_2SO_4$, 1072° C.

*Potassium carbonate,* $K_2CO_3$, acts same as $Na_2CO_3$ and is frequently mixed with it. A mixture in proportion to the molecular weights of the two substances is an excellent flux for decomposing certain silicates, clays, etc., which are difficult to handle by either carbonate alone. Melting point, $K_2CO_3$, 909° C.

*Potassium cyanide,* KCN, is a powerful reducing and desulphurizing flux and is frequently used in the fire assay of Pb, Sn, Bi and Sb. Its solution is a solvent of gold and silver. Fuses at red heat.

*Potassium hydroxide,* KOH, acts same as NaOH and is used for the same purposes. Melting point, 360° C.

*Potassium nitrate,* $KNO_3$, is a basic flux and also a powerful oxidizing agent. Melting point, 339° C.

*Sodium bicarbonate,* $NaHCO_3$, is a desulphurizing agent, a basic flux and sometimes an oxidizing agent. The corresponding potassium salt may also be used.

*Sodium carbonate,* $Na_2CO_3$, is used alone or in conjunction with other reagents for the decomposition of silicates, etc. Melting point, 849° C.

*Sodium chloride,* NaCl, a neutral flux, used as a cover in assay. Melting point, 804° C.

*Sodium hydrate,* NaOH, is used principally for the decomposition of sulphides and sulphates in sulphur determinations. Sometimes used

to decompose certain silicates, oxides and certain organic compounds. It is a basic flux. Melting point of NaOH, 318° C.

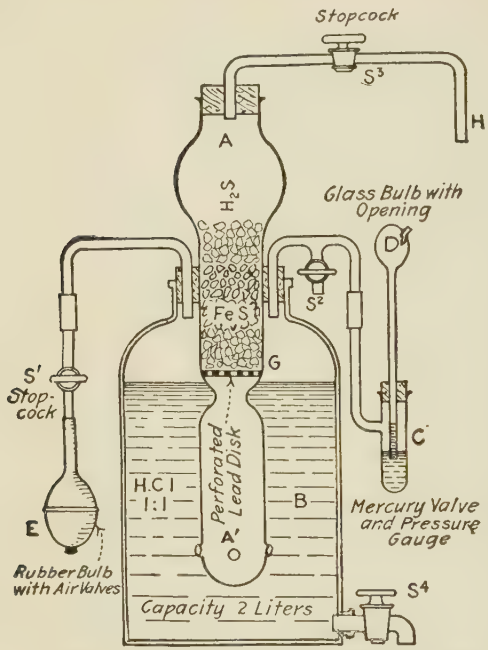



FIG 23*a*.—Scott's Hydrogen Sulphide Generator

*Sodium nitrate*, $NaNO_3$, is a decomposing and also an oxidizing agent. $KNO_3$ is also used for same purpose. Melting point, 316° C.

*Sodium thiosulphate* solution, $Na_2S_2O_3$, is a solvent for AgCl.

**Oxidizing Agents** in most general use are oxygen, chlorine, bromine, potassium permanganate, potassium bichromate, nitric acid, potassium chlorate, sodium nitrate, hydrogen peroxide and ammonium nitrate.

**Reducing Agents.** — Hydrogen, H, is used in the form of a gas which should be dry and free from impurities. Hydrogen sulphide, $H_2S$, is prepared by adding dilute $H_2SO_4$ to pure iron sulphide. If pure iron sulphide is not at hand it can be prepared by fusing iron nails with sulphur in the proportion of about 1 part iron to 2 parts sulphur, by weight. Sodium sulphite, $Na_2SO_3$, is used for the reduction of ferric solutions. It separates arsenious sulphide, which is soluble in it, from the sulphides of antimony and tin, which are insoluble in it. Stannous chloride, $SnCl_2$, is frequently used for reducing iron solutions. Solutions of sugar, tartaric acid and many other organic compounds will serve as reducing agents.

FIG. 23*a* shows a convenient form of a generator for obtaining hydrogen sulphide gas under pressure. The cylinder *A A'* is constructed, as shown, to support perforated lead disk *G*, upon which rests the iron sulphide. The lower end of the chamber is closed to catch small particles of FeS that may be carried through the perforations of the disk. Small openings admit the acid to *A'*. The level of the acid is below the disk *G*, so that the acid only comes in contact with the sulphide when pressure is applied by means of the rubber bulb *E*, the stopcock $S^1$ being open and $S^3$ closed. The mercury gauge *C* is adjusted to blow out at a given pressure, to prevent accident, the bulb *D* preventing the mercury from being blown out of the apparatus. A small opening in *D* allows the escape of the gas. When the apparatus is in operation, *H* is connected to an empty heavy-walled bottle, which in turn is attached with glass tube connection to the pressure flask in which the precipitation of the sulphide is made, the flask being closed to the outside air. By pressure on the rubber bulb *E*,

acid is forced into the chamber $A'$ past the disk into the sulphide in $A$. The entire system will now be under the pressure indicated by the gauge $C$. The pressure is released by opening the stopcock $S^1$ and the flask containing the precipitate then disconnected. The reservoir is designed to hold about two liters of acid, and the cylinder containing the sulphide is of sufficient capacity to hold over one pound of FeS, so that the apparatus will deliver a large quantity of hydrogen sulphide.

## PRECIPITATION

§ 30. 1. **Suggestion for Making Up Reagents.** — The reagents used in the laboratory for precipitating substances should have a known amount of compound per cc. It is very desirable that this factor be placed on the bottle. The reagents are commonly made on the loose percentage basis. For example, a 10% sodium oxalate solution is made by dissolving 10 grams of the salt in 100 cc. of water; a 10% sulphuric acid solution is often a 10% by volume solution, i.e. 10 cc. of the concentrated acid made up to 100 cc. with water. Such solutions are suitable for obtaining qualitative tests where exact quantities are not required, but for quantitative reagents it is far better to make these so that their values per cc. are known. For example, 10 grams of silver nitrate dissolved and diluted to 1000 cc. This would not be a 1% solution, but 100 cc. would contain 1 gram and 1 cc. value would be 0.01 g. $AgNO_3$. The chemist would now be able to use the necessary amount of reagent to accomplish intelligently the reaction desired. For decomposition purposes it is better for the chemist to make up his own reagents, as required, from the concentrated reagents on stock.

2. **Precipitation.** — The amount of reagent required should be estimated on the basis of such a percentage of constituent in the unknown as would exceed any possible amount that could reasonably be expected. If the material is one that contains uniformly given amounts, add sufficient reagent to precipitate the maximum quantity generally present and an excess of 10 to 25%. If a larger excess is necessary the amount will be indicated in the special method for the compound.

(*a*) *Example.* The unknown is a salt of barium which tests show to be barium chloride. One gram sample is taken. Now the percentage of barium in the pure salt, $BaCl_2 = (137.4 \times 100)$ divided by $137.4 + (35.5 \times 2) = 66\%$ barium. That is, 0.66 gram of barium may be present. If BaO is also present this percentage will be higher. The amount of barium would not exceed 0.8 gram unless the metal were present, a condition very unlikely. It would be safe to calculate the amount of reagent required on the basis of 0.8 gram of Ba being present. In the reaction that takes place all that need be considered in the calculation

$$\text{is } Ba + H_2SO_4 = BaSO_4$$

The other products formed do not matter here.

For every 137.4 grams of barium, 98.08 grams of sulphuric acid are required. The factor therefore of barium to sulphuric acid is obtained by dividing 98.08 by 137.4 which equals 0.7139. That is to say that 1 gram of barium will require 0.7139 of 100% sulphuric acid to completely react with it. 0.8 gram would require $0.7139 \times 0.8$ = a little over 0.57 gram and 10% excess will make this about 0.63 gram $H_2SO_4$ that should be added.

(*b*) If the reagent is marked 10%, this generally means 10 grams of reagent in 100 grams of solution. It is not customary to weigh out the acid. 1 cc. of this reagent actually contains about 0.107 gram of sulphuric acid (see Table X in back of book). If the reagent has been made by adding 10 grams of strong acid to 90 cc. of water it is nearer a 20% solution than 10%, and calculations should be made accordingly. Study examples § 17. If the reagent is correctly 10%, 0.63 divided by 0.107 will give the amount required to precipitate the barium, namely 6 cc.

(*c*) If the reagent is marked 1 cc. = 0.01 g. $H_2SO_4$ then since 0.63 gram is required, 0.63 divided by 0.01 = 63 cc. of reagent are required. In this case the acid is only about 1% in strength.

(*d*) **Addition of More Reagent.** — This is generally advisable if there is any doubt as to the amount being sufficient. After the precipitate has settled, a drop or so of the precipitating agent is added, and if any precipitation occurs a larger amount is added as required. If the strength of the reagent is not known it may be necessary to add this drop by drop as long as a precipitation is caused. Burettes should be used in general practice. In technical laboratories, where definite amounts are required, pipettes are convenient. It is a good practice to test the filtrate to be sure that the precipitation is complete. Review § 13 and § 14.

**Normality solutions.** — Should it be preferred to make up the solutions on the normality leases, using molecular weights in their relative combining ratios, it would be well to place of the reagent bottles the value in terms of one c.c. It should be remembered that a normal oxidizing factor weight may differ markedly from a precipitating factor weight. For example potassium dichromate as an oxidizing agent requires 73.55 grams per 1000 cc. of the salt, and 49.03 grams as a precipitating agent in a normal solution. A normal solution for gravimetric determinations and one for volumetric work might well be designated N — G. and N — V. following the exact value of the reagent.

*Examples.*

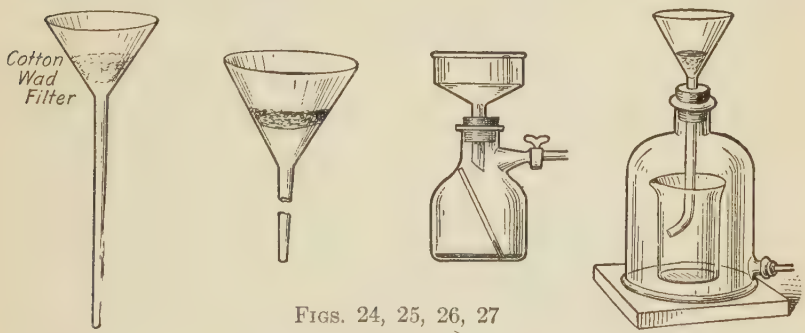
1.03 N × G. $K_2Cr_2O_7$ contains $1.03 \times 73.55$ g. per liter.
1.03 N × V. $K_2Cr_2O_7$ contains $1.03 \times 49.03$ g. per liter.

## FILTRATION

§ **31.** 1. The purpose of this is to separate the mother liquor and the excess of the reagent from the precipitate. If the precipitate is to be ignited and filter paper is used, this should be of a quality such as leaves practically a negligible weight of ash. For separations, where the precipitate is dissolved from the filter, the so called "ashless" filters are not necessary.

2. **Types of Filters for Rapid Filtration in Making Separations.** — A very simple type of filter for rapid filtration in separating out coarse material is what may be called the "*cotton wad filter.*" This is made by placing a loose ball of absorbent cotton in a funnel. The loose wad, about an inch or more in diameter according to the size of funnel used, is held in place and a stream of water poured over it. When freed from bubbles it will remain in place. Care should be used in not packing this wad, or allowing a tail of cotton to plug the stem of the funnel. See Fig. 24.

3. **Witt Plate with Paper Pulp.** — This type is used in connection




FIGS. 24, 25, 26, 27

with suction. The funnel is set up as shown in Fig. 25, the Witt plate is placed in the funnel and a paper filter slightly larger than the plate placed over it and moistened with water. Suction is now applied and a small amount of paper pulp [1] poured over the plate. This will close any leaks around the edge of the plate. The suction should be started before pouring any solution in this funnel otherwise the pulp will stir up and solid material will pass through. With long-stem funnel, suction is not required.

4. *The Büchner funnel* is convenient for filtration of large quantities of solution. It is used also with suction in connection with a filtering flask. See Fig 26.

5. *The Platinum Cone Filter.* — Where suction is desired in filtrations through the ordinary types of paper filters a platinum cone with perforations is useful for preventing the breakage of the paper.

[1] The pulp may be prepared by shredding filter paper in strong hydrochloric acid and then washing out the acid, using a Büchner funnel.

## FILTERING PRECIPITATES FOR IGNITION

6. *The Ordinary Filter.* — Directions for folding filters are given in the elementary courses in chemistry and will not be considered here. The Figs. 29*a* and *b* show the customary method of folding. The corner is torn off to make the filter fit more snugly around its upper rim in the funnel.

7. *Long-stemmed funnels* are recommended as they filter more rapidly owing to the suction caused by the column of water in the stem exerting a pull in proportion to its length. The writer has observed that etching or frosting the lower part of the funnel by means of hydrofluoric acid improves filtration. The frosted zone should be below the upper rim of the paper filter as this should adhere to a glazed surface to prevent air passing down the rim.

The stem of the funnels should rest against the side of the receiving beaker, otherwise the filtrate is apt to cause a splash that may result in loss.

FIG. 28

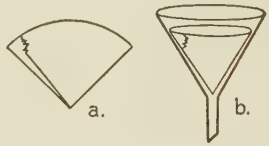



FIG. 29

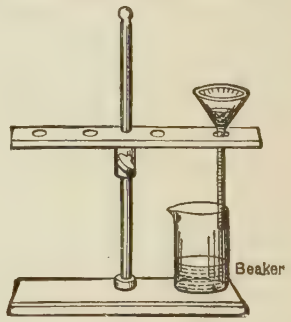



FIG. 30. Method of filtering.

8. *The Gooch Crucible.* — This is a popular form of apparatus for gravimetric determinations. The crucible prepared with an asbestos matt according to directions that follow is dried in an oven, and weighed. It is now used not only as a filter but also as a crucible in which the precipitate is ignited. This type of filter is desirable with precipitates that are reduced by the carbon of filter paper.

**§ 32. Preparation of a Gooch Crucible.** — 1. *Asbestos Fibre.* — The asbestos for use in Gooch crucibles should be carefully selected. The fibres should be moderately stiff, not the "cottony" type. Cut the fibre into pieces about $\frac{1}{4}$ inch long. Ignite the asbestos in a platinum dish at low red heat. Cool and transfer to a clean porcelain mortar and mascerate to a pulp with strong hydrochloric acid. Dilute with water and transfer to a large beaker containing 600–800 cc. of water. Stir thoroughly, allow to settle and pour off the milky water. Repeat the washing with water until the milkiness, due to powdered fibres, is scarcely evident. Now filter off the asbestos into a Büchner funnel. Again wash with water until free of acid. Transfer to a wide mouth bottle, add water in sufficient amount to form with the stirred up fibre a thin suspension of asbestos. This is now ready for use. If preferred the asbestos may be dried and kept in this form until desired.

2. *Preparation of the Filter.* — The Gooch crucible, either of platinum or porcelain, having a perforated bottom, is placed in a funnel tube and the apparatus set up as is shown in Fig. 31. The suction bottle holding the Gooch is attached to a second bottle, if a water filter pump is used to obtain the vacuum, as there is danger of water being sucked into the apparatus from the tap. Suction is now applied and a small amount of the finely suspended asbestos is poured into the crucible, in amount sufficient to form a thin pad of the material about $\frac{1}{16}$ inch thick over the bottom of the Gooch. The felt is washed with distilled water, the asbestos drawn down hard. It is possible to see light through the bottom of a properly made filter. The crucible is placed in an oven and the filter dried to constant weight at 110° C. For $BaSO_4$ and AgCl determinations it is advisable to make the filter

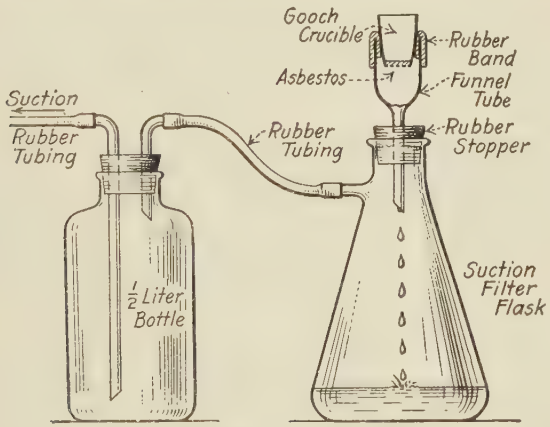



Fig. 31

about twice the above thickness to prevent the precipitate from passing through. Whenever the Gooch crucible is used, suction should be applied before pouring material into the crucible and the suction continued during the washing of the precipitate.

**§ 33. Filtration and Washing of Precipitates.** — In filtration and washing of the precipitate the following precaution should be observed.

(*a*) When filter papers are used the folds of the paper should be well creased to prevent the precipitate passing between the folds. The paper should fit the funnel snugly.

(*b*) The filter should not extend above the rim of the funnel.

(*c*) Wash out the greater amount of the mother liquor by using pure water in the first washings. If the filtrate is cloudy as it first comes through, pass this portion again through the filter.

(*d*) To prevent cloudy filtrates, add the precipitating agent slowly to a hot solution. Allow to stand, stirring occasionally, until

the "digestion" forms crystals which will not pass through the filter.

(*e*) Precipitates that persist in passing through the filter may often be prevented from doing so by adding to the wash water an ammonium salt, such as ammonium chloride or ammonium nitrate. The salt need not be washed out as it is volatile. The salts prevent formation of colloids.

(*f*) Test the filtrate to ascertain whether the precipitation has been complete. With experienced analysts this precaution is not necessary.

(*g*) Gelatinous precipitates filter slowly and are difficult to wash free of impurities occluded by the precipitate. Filtration may be hastened by adding paper pulp to the solution containing the precipitate or by pouring a little paper pulp into the filter before adding the filtrate.

(*h*) Washing by decantation is generally to be recommended, as much as possible of the precipitate being retained in the beaker during the first three or four washings and the precipitate then transferred to the filter. This treatment is unnecessary for crystalline, easily filtered precipitates.

(*i*) Precipitates which absorb (occlude) substances should be redissolved and the precipitation repeated. This is especially necessary in separations where the substance, liable to be absorbed, is being determined.

(*j*) The beaker in which the precipitation was made should be "copped" out and all the material transferred to the filter, the beaker being left perfectly clean.

(*k*) To ascertain whether impurities have been washed out from the precipitate precautions are generally given to test the wash water. For example, in washing barium sulphate free of the excess of barium chloride reagent, in the determination of sulphur, tests are made for chlorine. This precaution is excellent advice for the beginner. It is never observed by the experienced chemist as thoroughly tested methods for removal of impurities have made ample provision for removal of such impurities.

(*l*) A filter is best washed by starting with a stream of the wash water around the upper rim of the filter and following down in a spiral towards the precipitate in the apex, filling the filter $\frac{1}{2}$ to $\frac{2}{3}$ full at each washing.

(*m*) Washing the precipitate with hot water or when necessary with hot water and a volatile salt with an ion common to one of the precipitates is frequently advisable. For example, lead sulphate, $PbSO_4$, is prevented from dissolving by adding sulphuric acid, $H_2SO_4$, to the wash water. Likewise the precipitate potassium cobalt nitrite, $K_6Co_2\ (NO_2)_{12}$, is washed with a 10% solution of potassium acetate, $KC_2H_3O_2$, containing potassium nitrite, $KNO_2$, and ammonium phosphomolybdate is washed with ammonium nitrate. See § 7. Hot water is especially advisable in washing gelatinous precipitates such

as ferric hydroxide, aluminum hydroxide, uranium hydroxide, etc. Addition of ammonium salts such as ammonium nitrate also prevents formation of colloidal solutions.

(*n*) Occasionally it is necessary to wash the precipitate with a wash solution that has been saturated with the same compound (e.g. Determination of platinum).

## IGNITION

§ **34.** 1. The purpose of ignition of the precipitate that has been separated from its mother liquor and the excess of precipitating re-

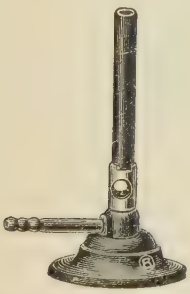


FIG. 32 — Bunsen Burner

FIG. 33 — Meker Burner

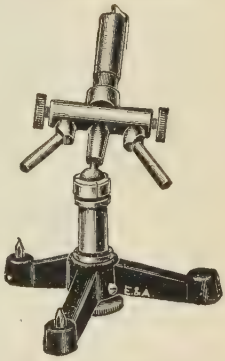


FIG. 34 — Blast Lamp

agent, is to expel the water present free or combined, and to form a compound of definite composition.

2. The amount of heat necessary varies with the compound, from the heat of the drying oven (100° C.) through the dull red heat to white heat of the blast lamp.

I. **Apparatus.** — 1. *Various types of burners* are commonly used; the Bunsen burner, Fig. 32; the Meker or Scimatico burner, Fig. 33; the blast lamp, Fig. 34, are familiar types; the order named is in direct ratio of heats obtained. With a good grade of gas the Bunsen gives a temperature of about 1100° C. while a blast lamp gives over 1800° C. The heat value depends largely on the grade of gas used and the construction of the burner. In the study of the gas flame it has been learned that the flame may be considered as being made up of zones, the cold inner gas zone, of un-

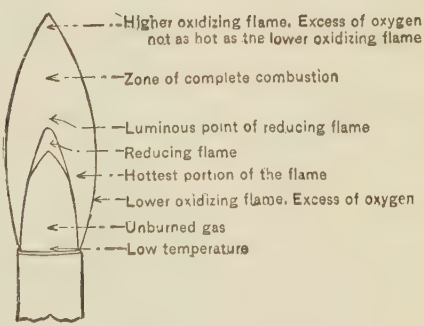

Higher oxidizing flame. Excess of oxygen but not as hot as the lower oxidizing flame
Zone of complete combustion
Luminous point of reducing flame
Reducing flame
Hottest portion of the flame
Lower oxidizing flame. Excess of oxygen
Unburned gas
Low temperature

FIG. 35 — Gas Flame

burned gas, the zone of high heat with the reducing flame, the zone of complete combustion. See Fig. 35. The Meker burner flame, by an ingenious device of a large number of small openings is made up of a corresponding number of flames, thus practically eliminating the cold

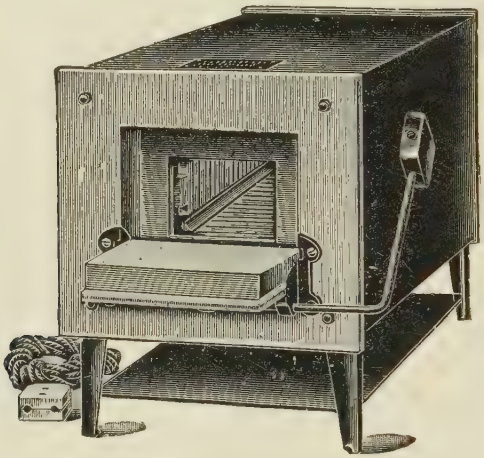


Fig. 36 — Electric Furnace

inner zone of unburned gas, resulting in a more intense heat. This type of burner meets the greatest demand in ignitions. The blast lamp utilizes additional air for combustion of the gas, thus eliminating the colder gas zone. This type of burner is required in blasting precipitates from which water is driven with great difficulty, as in case of aluminum hydroxide, which requires intense heat to form the oxide of definite composition ($Al_2O_3$). The electric furnace may be used in place of burners for strong ignitions. Fig. 36.

Fig. 37 — Platinum Crucible

2. *Crucibles.* — Porcelain, silica, alundum, "rotanium"[1] and platinum crucibles are familiarly known in the technical laboratory. Porcelain, silica, and alundum are useful where an intense heat is not required; platinum is especially useful for high temperature ignition heats, where the blast lamp is required. See Figs. 37, 38.

Fig. 38—Porcelain Crucible

[1] Jour. Ind. Eng. Chem. Vol. 9. No. 9, p. 590. June, 1917.

II. **Care of Platinum.** — When using platinum the following *precautions* should be observed: —

(*a*) Platinum should not be handled at red heat with iron or nickel tongs; this should be done only with platinum tipped tongs, otherwise the platinum should be slightly cooled before removing from the triangle, the flame being removed.

(*b*) Platinum should not remain in contact with the inner unburned gas zone or in contact with a smoky flame as the carbon present in the flame will alloy with the crucible, forming a brittle carbide. See that the hot colorless flame alone is in contact with the vessel.

(*c*) Do not ignite in platinum the elements or compounds of arsenic, antimony, tin, lead, bismuth, and zinc; free sulphur or phosphorus or compounds of these easily reduced by the carbon of a filter.

(*d*) Never handle platinum roughly by bending it or attempting to remove adhering substances with a file, or glass rod or other hard material. Such substances should be dissolved out with hydrochloric or nitric acid, never the two together as the metal dissolves in aqua

Fig. 39 — Pipestem Triangles

regia; it is also attacked by hot alkalies, such as sodium and potassium hydroxides; it is attacked by bromine, iodine, and chlorine, so that in dissolving out precipitates avoid using reagents which would liberate the halogens. Some substances which resist hydrochloric acid may be removed by fusion with sodium carbonate or potassium acid sulphate. See §§ 45 and 46.

(*e*) In polishing platinum to keep it bright, as it should be kept, use sea sand; the grains are rounded and will not scratch the metal.

(*f*) To keep the vessels from being bent, wooden moulds are often used. Platinum ware should be kept in a box by itself.

III. **Procedure in Ignitions.** — 1. The crucible should be heated to redness, by placing it on a pipestem triangle, or a nichrome or platinum triangle, resting on a tripod under which is the burner. (Fig. 38 and Fig. 39.) The crucible is cooled in a desiccator, then weighed and its weight recorded.

2. The material is placed in the crucible by pressing the top of the filter together, giving the upper portion a fold, to safely enclose the precipitate, then inverting the filter so the apex stands up in the crucible. There are two methods of igniting the precipitate.

(*a*) Ignition of the precipitate in the filter while still moist (a wet filter and precipitate being dried slightly before ignition). This is done with precipitates which are not liable to serious reduction by the carbon of the filter.

(*b*) By drying the filter and precipitate, removing as much as possible of the compound from the filter, placing it on a sheet of glazed paper, then igniting the filter, the precipitate is now added to the ash of the filter in the crucible and it is ignited.

3. The length of ignition depends upon the nature of the substance. Barium sulphate, for example, should not require over 10–15 minutes, while aluminum hydroxide will require half an hour or more of blasting to effect the desired results. It is well to start with a low heat, i.e. cover the crucible and apply heat gradually, then more strongly to full heat of burner or blast, with crucible uncovered.

4. The crucible tilted on its side enables air currents to enter the vessel to oxidize the filter paper carbon. (Drafts should be avoided as the material may be blown out.)

5. The crucible is placed in a desiccator and cooled and then weighed. Fig. 40.

6. The ignition is now repeated for a few minutes and the material again cooled and weighed. This is repeated as long as a loss of weight occurs. The compound should become constant in weight.

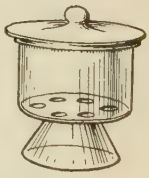


Fig. 40 — Desiccator

7. *Oxidation of Carbon Resisting Combustion.* — Occasionally carbon is held within the precipitate and resists oxidation as the material has fused around it protecting the carbon from the air. This is often the case in ignitions of magnesium phosphate. Oxidation may be effected by moistening the cooled residue in the crucible with strong nitric acid, heating gently to expel the acid and then strongly.

**§ 35. Standardization of Weights and Volumetric Apparatus.** — For accurate work it is important that the standards by which we make our estimation — weighing and volumetric measuring — be accurate. Details for standardization of weights and volumetric apparatus are given in a special chapter on the subject under "Apparatus."

**§ 36. Precautions in Volumetric Analysis.** — The following facts should be noted in volumetric determinations:

(*a*) The measuring vessels, pipettes, volumetric measuring flasks and burettes should be clean. Potassium dichromate-sulphuric acid reagent is excellent for removing grease and cleaning this apparatus. (See Reagents.) Special attention should be given to burettes draining properly, i.e. drops of the reagent should not cling to the walls of the burette during a titration. If this occurs the results obtained will not be accurate.

(*b*) The conditions under which the reagents are used should be

the same as those of standardization. For example, a reagent standardized at 25° C. will not have the same value per cc. as it will at 15° C. An allowance must be made for contraction in this case. Like gases, liquids contract on cooling and expand on heating; unfortunately no definite rule can be given for all solutions, as the contraction and expansion are influenced by the nature of the liquid. Furthermore, the expansion, unlike gas, is not constant per degree. (Consult Table CXLV, p. 629, Van Nostrand's Chemical Annual — Olsen Fifth Issue.) Correction factors will be given for the reagent where deemed necessary (e.g. Chapter on Acidimetry and Alkalimetry).

(*c*) The same amount of indicator used in standardization should be used in the subsequent titrations with the reagent.

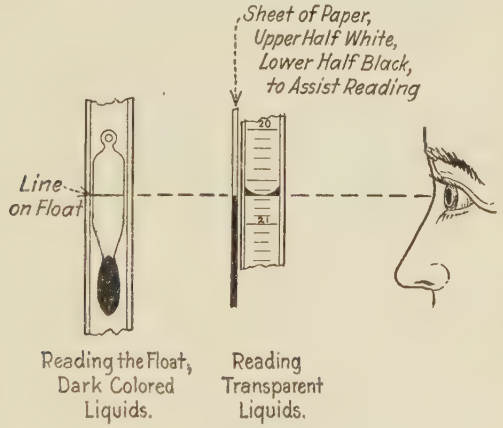

Sheet of Paper, Upper Half White, Lower Half Black, to Assist Reading
Line on Float
Reading the Float, Dark Colored Liquids.
Reading Transparent Liquids.

Fig. 41

(*d*) The standard solutions should be kept in air-tight glass stoppered bottles. Some reagents should be kept in dark glass bottles.

(*e*) Standards should be checked occasionally, the frequency necessary varying with the reagent. This will be taken up again under "Preparation of Reagents."

(*f*) Before titration it is necessary to shake up the standard solution, to make the mixture uniform, since some vapor may condense on the walls of the bottle, which should be included with the reagent.

**Reading of Burettes.** — The Fig. 41 shows the position of the eye in reading a burette. Floats are convenient for opaque liquids such as iodine.

## ANALYSIS

**§ 37. Preliminary Considerations — Moisture and Water of Crystallization.** — The samples as received may contain considerable moisture that cannot be neglected in the evaluation of the product.

Ores, for example, shipped in open cars, may pick up water in transit from the mines of producer to the customer. This water content should be determined at the mines as well as at its final destination.

## DETERMINATION OF MOISTURE AND WATER OF CRYSTALLIZATION

1. **Moisture.** — The moisture is best determined on a 10–100 gram sample. The sample is weighed and placed in a watch or clock glass and heated to constant weight in oven at 105–110° C. The loss of weight is calculated to per cent on a 10 gram sample by multiplying by 10 and directly on 100 gram sample.

2. **Water of Crystallization.** — Many of the crystallized salts do not give up all of their water of crystallization until heated considerably above the boiling point of water. Two methods of procedure will be considered.

(*a*) *The Loss Method,* which consists in heating the salt to a temperature at which the water is completely driven off and obtaining the loss of weight by weighing the anhydrous salt. By this method error may result owing to the fact that the anhydrides generally absorb moisture rapidly from the air, so that the salt must be transferred hot to the desiccator, cooled and then weighed as rapidly as possible.

(*b*) *Absorption or Direct Method,* which consists in heating the salt in a boat in an enclosed tube, passing a current of dry air over the sample which carries the moisture to a tube containing a dehydrating agent, where the water is absorbed and may be weighed directly.

3. **The Loss Method in Detail.** — For practice a sample of either barium chloride or copper sulphate will be taken. $BaCl_2.2H_2O$, $CuSO_4.5H_2O$. The determination should be made in duplicate.

*Procedure.* — Carefully clean and dry a weighing bottle. Place in this 5–10 grams of the crystals. If the crystals are large they should be broken down to about the consistency of coarse sand.

Heat the crucible on a pipestem triangle to redness and cool the crucible in a desiccator containing calcium chloride. Weigh and record the weight in a notebook.

Place in the crucible 1–2 grams of the sample from the weighing bottle. Make note of the exact amount by deducting the weight of the crucible from the total weight of crucible and salt.

Place the crucible in a clean crucible of iron or nickel of sufficient capacity to allow an air space of $\frac{1}{4}$ inch around the vessel containing the salt. A thin asbestos pad is placed at the bottom of the larger crucible separating it from the smaller.

Place the larger crucible with its contents on the triangle of a tripod and heat to low redness, applying the heat gradually, keeping the temperature within the crucible at 100–120° C. for 10 minutes or more,

then increasing to 250° C., the outer crucible becoming red hot. Keep the large crucible at red heat for about 10 minutes.

Cool in a desiccator and then weigh the smaller crucible with its contents and note the loss of weight.

Repeat the heating in the larger crucible until the weight of the sample becomes constant. Calculate the loss of weight and report as per cent water. (Loss × 100 divided by Wt. taken.)

*Note:* It is frequently necessary to cover the inner crucible during the initial heating to prevent loss of salt due to "snapping out," decrepitation. The crucible cover should also be weighed.

**§ 38. Determination of Water. Absorption Method.**[1] — The apparatus for this determination is shown below. (Fig. 42.) The combustion tube *C* is attached to the calcium chloride or phosphorus pentachloride tubes *A* and *D*. The former to dry the air entering *C* and

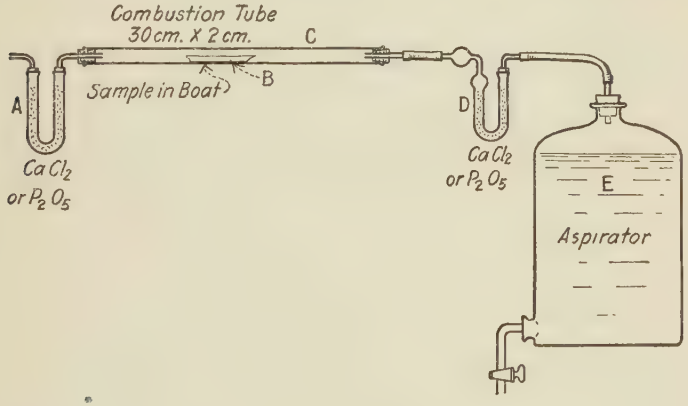



Fig. 42

the latter, *D*, to retain the moisture swept from the sample in the boat *B*. The carboy *E* is used as an aspirator by allowing an outflow of water (about five drops per second) from a stopcock at the bottom.

*Procedure.* — The combustion boat *B* is dried and weighed. Meantime the apparatus is swept out with dry air for about 10–15 minutes.

The tube *D* is detached and carefully weighed, preferably using a counter-weight calcium chloride or phosphorus pentachloride tube, which is kept alongside of *D*. The tube *D* contains calcium chloride in small lumps. The ends of the tube are packed loosely with cotton or glass wool. Tube *A* is prepared in the same way.

Place in *B* 1–2 grams of the sample. Insert in the tube *C*. Attach the weighed tube *D*. See that the apparatus is properly connected and tight.

Gently apply heat to the portion of the tube adjacent to *B*. In-

[1] These methods are not applicable to compounds decomposing on heating.

crease the heat as desired by means of a Meker burner, aspirating air through the apparatus by allowing an outflow of water from $E$ at the rate of five drops per second.

If any moisture condenses in $C$ drive it forward to $D$ by heating the tube, but be careful not to heat the tube too much near the rubber stopper, as fumes from the rubber would cause an error in results.

Forty minutes to an hour should be ample for the expulsion of water. The temperature finally obtained should be not over 300° C. for most salts. Higher heat may be necessary for certain oxides, but for such the ignition method in an open crucible is recommended.

The tube $D$ is disconnected and weighed. (Using the tare weight counter balance, as suggested.) The increased weight is due to the water of the sample.

**Calculation of Percentage of Material Determined in the Original Sample to the Dry Basis, or if Determined on a Dried Sample to the Original Form Including Water.** — Frequently a chemist is required to report the percentage of constituent both on the dried sample and in its original form containing water. The following formulae will be of assistance in these calculations.

Let $a$ = percentage of material found (determined on the dry basis, or in the original sample, as the case may be).
$b$ = percentage of total dry material with water expelled.
$c$ = percent of water in the original sample, $100 - c = b$.

Then $\frac{100 \times a}{b}$ = Percent calculated from wet basis to dry.

$\frac{a \times b}{100}$ = Percent calculated from dry basis to wet.

## DETERMINATION OF MOISTURE IN GASES

**§ 39.** The gas to be tested is passed through a dehydrating agent such as phosphorus pentoxide, $P_2O_5$, alumina, $Al_2O_3$, or lime, $CaO$, contained in a weighed U-tube, Fig. 43. The following facts should be borne in mind in selecting the dehydrating agent: (*a*) It should not absorb the gas; (*b*) it should not react chemically with the gas. For example — lime or alumina could not be used for determining moisture in sulphur dioxide, nor could phosphorus pentoxide be used in determining moisture in ammonia. For the former, phosphorus pentoxide is best, and for the latter, lime. Alumina that has been carefully heated to 1400° is useful for determining moisture in neutral gases. It should be remembered that gases dried over calcium chloride will give up moisture to strong sulphuric acid, and these in turn will give up moisture to phosphorus pentoxide: Professor Morley has even determined the amount of moisture that is left after this latter treatment.

**Procedure.** The volume of the gases required for the test varies widely according to the percentage of moisture in the gas, 1000 cc. to 10,000 cc. are generally required. For minute amounts of moisture

it may be necessary to lead the gas over the dehydrating agent for a given length of time, using a manometer or difference gauge, or a gas meter. The absorption tube is weighed before and after the test and the increase in weight taken as the moisture content of the gas.

## SUGGESTIONS

**§ 40.** Read the Introduction to become familiar with the subjects discussed. Know, at least, where to find the subjects with which it deals. Review these special sections as required during the course of study.

In the body of the text the elements are taken up in alphabetical order, but it is not advisable to make a study of these in the order presented. The arrangement is for convenience of reference, as is also the arrangement of the topics in each chapter. The following outline is generally adhered to in each chapter.

### Element

A. (*a*) *Detection.* — Qualitative tests — For information, when desired.
(*b*) *Estimation.* — Preparation of the sample. Suggestions regarding methods of solution of substances commonly examined for the element under consideration. This section is intended for general reference, for special cases that come within the scope of a technical laboratory.
(*c*) *Separations.* — This section also is for reference, to afford information that may be drawn upon for special cases.

B. *Methods.*

Here are given the details of procedures which may be generally used. Optional methods are included to meet local conditions. Certain methods are recommended for the beginner on account of the simplicity of the procedure and the added detail, explanation of reactions, etc.

The methods are classed under two heads — gravimetric and volumetric. The procedures have been carefully selected from recognized standard methods that are rapid and accurate.

**§ 41.** The following courses are recommended. Study the elements in the order given.

### I. Elementary Course for Beginners

*Gravimetric Methods:*

Water of crystallization,
Chlorine and silver,
Calcium and carbon dioxide (limestone),
Aluminum and iron (determined as oxides),
Magnesium (determined as pyrophosphate),
Ash and volatile matter in coal,
Copper by electrolysis,
Silver by electrolysis,

*Volumetric:*

Review sections on volumetric analysis in Introduction
Acidimetry and alkalimetry,
Sulphuric acid and sodium hydroxide,
Sodium carbonate determining sodium hydroxide as well as carbonate,
Sodium bicarbonate, determining also the sodium carbonate present,
Calcium by permanganate method,
Iron by chromate and permanganate methods,
Manganese by the oxalate-permanganate method,
Lead by the oxalate-permanganate method,
Copper by the iodide method,
Arsenic by the iodine method,
The Gutzeit method for traces of arsenic,
Antimony by the bromate method,
Zinc by the ferrocyanide method,

## II. Advanced Course in Quantitative Analysis

The student has had both gravimetric and volumetric methods. In this course a study is made of the less common elements using the method best suited for the purpose. A study is made of special subjects as the demand may arise. The following order of subjects is offered by way of suggestion.

Silver, gravimetric and volumetric,
Nickel, gravimetric and volumetric,
Chromium, the iodide and ferrous sulphate methods,
Molybdenum, gravimetric and volumetric,
Tungsten, gravimetric method,
Uranium, gravimetric method,
Vanadium, volumetric method by permanganate,
Cobalt, mercury, tin may also be studied.

*Special Subjects.* The analysis of steel for
Sulphur, Manganese, Carbon and Phosphorus, and Silicon in iron; the following methods being recommended.
Evolution and gravimetric methods for sulphur,
Bismuthate method for manganese,
Colorimetric and combustion methods for carbon,
Alkalimetric method for phosphorus,
Silicon in iron,
*Alloys*, determination of lead, antimony, tin, zinc, etc.
*Slags* and flue dust
*Impurities* in refined copper
*Impurities* in refined lead
*Impurities* in alloys.

III. Special Courses

Fire Assay Methods
Analysis of Gas
Analysis of Water
Other Special Courses
Research Investigations.

## DEMONSTRATION METHOD FOR LABORATORY INSTRUCTION

A marked advance in the efficiency of laboratory instruction has been attained by the demonstration method,[1] a procedure calling upon the teaching ability of the instructor. The smaller the class or section, the better for the individual student. The following is an outline of the method: —

At the outset such methods are selected as can be completed in a single laboratory period of three hours. The students are provided with notes in which the analytical procedure is divided into short natural consecutive steps, indicated as 1, 2, etc. All the students are provided with portions of the same sample, and in the demonstration stage it is immaterial whether the correct result of the determination be known in advance or not. The instructor, at his own conveniently situated desk, gathers the students around him and runs rapidly through the notes, calling attention to the general procedure and giving such brief explanations as appear advisable for intelligent work, but no extended considerations of reactions or theory, these being reserved for a subsequent lecture. Now, with a previously weighed out portion of the sample, he goes through the first step, demonstrating the proper manipulation and calling attention to every detail. The students are then sent to their desks to duplicate what they have just seen, but to proceed no further. When all have finished the first step, the second step is similarly demonstrated and duplicated, and so on to the end. The results attained are surprisingly accurate. While the students are working, the instructor goes among them supervising, this being very easy as all the students are doing the same thing at nearly the same time.

The step method has succeeded where demonstration of the entire method at once has failed. With the step method the student tries a thing before he forgets it, and the trial then fixes it in his memory. He quickly learns to observe and to manipulate correctly. His success develops an intelligent interest in his work and his mind becomes trained to logical thought.

At the next lecture period all necessary explanations relative to theory, reactions and calculations are given in detail. This has proven

[1] Method developed by Dr. A. H. Low, Colorado School of Mines.

to be better than giving the lecture before the laboratory period, as the student recognizes and better visualizes the various details of the analysis as they are referred to and his interest is less liable to fag. Students beginning a quantitative course are presumed to possess sufficient chemical knowledge to enable them to work intelligently in the laboratory with only the brief preliminary explanations given at the time, coupled with the demonstrations of the instructor.

As proficiency in manipulation, observation and logical thought is attained, the above procedure is varied by the omission of the demonstration of familiar steps, until, finally, the notes alone are all that the student requires. Unknowns are substituted for knowns at any time the instructor deems advisable.

### Illustration. Manganese in Ores, Oxalic Acid Method [1]

1. 0.5 gram of ore in 8-oz. copper flask. With oxides, add 10 cc. of HCl and heat gently. With sulphides or mixed ores, follow the HCl shortly with 5 cc. of nitric acid. Heat gently until decomposition is complete, then add 5 cc. of $H_2SO_4$ and heat over a free flame almost to dryness. Allow to cool, add about 100 cc. of water, heat to boiling and then allow to stand, hot, shaking occasionally, until any anhydrous ferric sulphate has dissolved.

2. Add 1 or 2 grams of zinc oxide (fine, not lumpy) and heat to boiling. Remove from heat and continue to add zinc oxide in small portions, while shaking, until all iron is precipitated and a moderate amount of zinc oxide remains in the bottom of the flask. Heat to boiling (liable to foam) and then filter through an 11 cm. filter having a small wad of wetted absorbent cotton in the apex. Wash ten times with hot water, receiving the filtrate in a 500 cc. beaker. If any lead is liable to be present, add 2 cc. of saturated $K_2Cr_2O_7$ solution before boiling.

3. Add to the filtrate 3–4 grams of sodium acetate, or about 5 cc. of a saturated solution, and 25 cc. of saturated bromine water. Heat to boiling and boil several minutes. If bromine vapors do not appear above the liquid in the covered beaker, add more bromine water until they do. This shows the necessary excess. Now filter through an 11 cm. filter and wash ten times with hot water. Any $MnO_2$ adhering to the beaker is simply washed clean and left there. It will be recovered later. The filtrate should be clear.

4. Place the filter containing the washed precipitate back in the beaker and run in from a burette what is judged to be an excess of standard oxalic acid solution. 1 cc. of this titrates about 1% of Mn, on the basis of 0.5 gram of ore taken. Now add about 50 cc. of $1:10 H_2SO_4$, heat to boiling and then allow to simmer gently (to avoid shredding the filter) with occasional stirring, until

[1] $MnO_2$ reduced to MnO by $H_2C_2O_4$ — hence Mn = O — 1 cc n./10 reagent = 0.00275 g. Mn.

the precipitate has completely dissolved, adding more of the standard oxalic if necessary, but avoiding a large excess. Note the total amount used.

5. Dilute the hot solution with about 200 cc. of hot water and titrate to a faint permanent pink tinge with standard potassium permanganate solution, remembering that the filter paper will slowly destroy the pink tinge after the end-point is reached.

6. Multiply the cc. of permanganate used by the factor to convert it to its value in cc. of the oxalic acid employed. Deduct this from the total cc. of oxalic acid used and multiply the remainder by the percentage value of 1 cc. of the oxalic acid in Mn.

*Keeping of Note Books.* — Insist upon the use of note books for recording all weighings, results of titrations, and calculations. The use of loose scraps of paper for recording results and for making calculations encourages "sloppy" work and should be prohibited.

# PART II

## ANALYTICAL METHODS

### ALUMINUM [1]

**Al, at.wt. 27.1; sp.gr. 2.58; m.p. 658.7°C.; b.p. 2200° C.; oxide, $Al_2O_3$.**

Aluminum is determined in a great variety of substances, in ores, cements, plaster, ceramic materials, in which it is generally reported as $Al_2O_3$. It is determined in aluminum salts, in the control of processes in the manufacture of aluminum products; in aluminum metal and its alloys,[2] in which it is reported as metallic aluminum.

#### OCCURRENCE

Aluminum occurs only combined in nature. It is the most abundant of the metals, composing nearly 8% of the earth's crust. It is an essential substance of practically all of the siliceous rocks, the feldspars, zeolites, chlorides, micas, mica schists, granites, porphyry, slate, clay, obsidian (pumice stone), tourmalin, etc.

**Minerals.** — The more important of the minerals are the following:

*Bauxite*, $Al_2O_3.2H_2O$, a mineral of commercial importance, with fine grained or sponge-like to clay-like mass; white color if pure but more often colored by iron a yellow to red depending upon the amount of iron present; lustre dull or earthy; streak the same as the color of the mineral; opaque; brittle; hardness 1–3.

*Cryolite*, $Na_3AlF_6$; vitreous lustre; transparent to translucent; colorless, white or brown; white streak; brittle; hardness 2.5.

*Corundum*, sapphire, ruby, emery, $Al_2O_3$. Vitreous to adamantine lustre; transparent to opaque; blue, red, green, yellow, black, brown or white; brittle to tough; hardness 9.

Other minerals — *Spinel*, $MgO.Al_2O_3$; *Diaspore*, $Al_2O_3.H_2O$; *Gibsite*, $Al_2O_3.3H_2O$; *Cyanite*, $Al_2SiO_5$; *Topaz*, $(Al(F,OH))_2SiO_4$; *Andalusite*, $Al_2SiO_5$; *Sillimanite*, $Al_2SiO_5$; *Staurolite*, $(AlO)_4(AlOH)Fe(SiO_4)_2$; *Kaolinite*, $H_4Al_2Si_2O_9$; *Pyrophyllite*, $H_2Al_2(SiO_3)_4$; *Wavellite*, $4AlPO_4.2Al(OH)_3.9H_2O$; *Turquois*, $CuO.3Al_2O_3.2P_2O_5.9H_2O$; *Alunite*, $K_2Al_6(OH)_{12}(SO_4)_4$; *Crysoberyl*, $BeO.Al_2O_3$.

[1] Also spelled Aluminium. Suggestions for experimental work, page 76.
[2] Ferro-aluminum. Substances in alloys Si, Mn, S, P, C, Cu, Na, Fe.

## DETECTION

**General Procedure.** — The sample is brought into solution. Silica is removed by taking the solution to dryness, boiling the residue with hydrochloric acid and filtering. The members of the hydrogen sulphide group are removed as usual with $H_2S$, the filtrate boiled to expel the excess of $H_2S$, iron oxidized with nitric acid, and aluminum, iron and chromium precipitated as hydroxides by addition of ammonium hydroxide in presence of ammonium chloride. On treating the precipitate with sodium peroxide, aluminum and chromium hydroxides dissolve, whereas ferric hydroxide remains insoluble. Aluminum hydroxide is precipitated by acidifying the alkaline solution with hydrochloric or nitric acid, and neutralizing with ammonia; chromium remains in solution.

**Cobalt Nitrate Test.** — The white gelatinous precipitate of aluminum hydroxide may be confirmed by adding a drop of cobalt nitrate solution and burning the filter. The residue will be colored blue by the resulting aluminum cobalt compound.

**Sodium Thiosulphate Test.** — $Na_2S_2O_3$, added to a neutral or slightly acid solution, containing aluminum, precipitates aluminum hydroxide, upon boiling the solution. Sodium sulphite, or ammonium chloride added in large excess, will also cause this precipitation.

**Alizarin S. Test.** — The reagent used is a 0.1% filtered solution of commercial alizarin S, the sodium salt of alizarin monosulphonic acid (yellow with acids, purple with alkalies).

To 5 cc. of the neutral or acid solution under examination is added 1 cc. of the reagent, and then ammonia until the solution is alkaline, as shown by the purple color. The solution is boiled for a few moments, allowed to cool, and then acidified with dilute acetic acid, when red coloration or precipitate remaining is conclusive evidence of the presence of aluminum. The red calcium, strontium, barium, zinc and magnesium salts, and salts of other metals later than Group II are readily soluble in cold dilute acetic acid, and do not interfere with the coloration.

Phosphates or chromium do not interfere and comparatively large amounts of iron may be present (0.003 milligram Al in presence of 1 milligram ferric iron, 10 milligrams chromium salt). In presence of greater quantities of iron citric acid is added to keep this in solution. One part of aluminum may be detected in 10 million parts of water.

## SUGGESTIONS FOR EXPERIMENTAL WORK

Aluminum is generally determined gravimetrically. The amateur is advised to start with an aluminum salt with known composition, such as potash alum, $Al_2(SO_4)_3.K_2SO_4.24H_2O$, containing 5.71 per cent of aluminum. In this case a 5 gram sample should be taken and the salt dissolved by addition of 150–200 cc. of hot distilled water

(solubility 5.2 g. per 100 cc. at 0° C. Readily soluble in hot water) Since no interfering elements are present the aluminum hydroxide may be precipitated immediately with ammonia according to the first of the gravimetric procedures, page 78.

Following the practice with the water soluble aluminum salt a more difficult compound may be undertaken, such as bauxite. It will be necessary to effect decomposition by a procedure given on page 78, preferably the General Procedure for Ores. Since silica and iron are invariably present a separation must be effected as given under "Notes" page 80. Should a phosphate be present either a separation must be made or the aluminum precipitated as a phosphate by the second gravimetric method given on page 83. This method is generally used in the gravimetric determination of alumina in presence of iron, and is applicable to the determination of aluminum in iron and steel. It is advisable to consult the notes on the determination of aluminum given on page 80.

### Preparation and Solution of the Sample

Full details for preparation of the sample are given on the following page under the gravimetric method for determining aluminum so that a preliminary survey of the subject is deemed unnecessary here. See also § 28 in the chapter "Introduction".

**Separations.** See "Notes" page 80.

## GRAVIMETRIC METHODS FOR THE DETERMINATION OF ALUMINUM

There are two general procedures for the gravimetric determination of aluminum: *A*. Direct determination, when it is possible to precipitate the hydroxide or phosphate of the element free from impurities. *B*. Indirect determination, when the element is precipitated and weighed along with iron, the latter then being determined by titration and the aluminum estimated by difference.

### DETERMINATION BY HYDROLYSIS OF AN ALUMINUM SALT WITH $NH_4OH$

**Principle.** — The method depends upon the hydrolysis of a soluble salt of aluminum by neutralizing the free and combined acid with ammonia. This hydrolysis takes place in the presence of ammonium chloride, which prevents the precipitation of magnesium hydroxide by $NH_4OH$, the common ion $NH_4$ repressing the ionization of the base $NH_4OH$. (See Notes.) The direct determination of aluminum by this procedure excludes the presence of the elements undergoing hydrolysis with similar conditions. Iron, chromium, titanium, zirconium, thallium, cerium, interfere. In their presence a separation must be made.

**Reaction.** — $AlCl_3 + 3NH_4OH = Al(OH)_3 + 3NH_4Cl$.

If phosphoric acid is present in the solution aluminum will be precipitated as the phosphate, $AlPO_4$.

**Reagents.** — Ammonium hydroxide, ammonium chloride, hydrochloric acid, ammonium nitrate solution (20 cc. $HNO_3$ diluted and neutralized with $NH_4OH$ and then diluted to 1000 cc.).

**Procedure.** 1. *Preparation of the Solution.* — In dissolving substances containing aluminum it will be recalled that the oxide, alumina, although ordinarily soluble in acids, is very difficult to dissolve if strongly ignited, likewise alumina in certain combinations, with silica and potassium, in clays, etc., does not yield readily to acid treatment. Such compounds are best decomposed by fusion with sodium and potassium carbonates (see Introduction, § 36) or acid potassium sulphate. The latter fusion may be conducted in " Low's " pear-shaped flask.

*General Procedure for Ores. Acid Treatment.* — One gram of the finely powdered ore is treated in a platinum dish with 5 cc. of concentrated sulphuric acid (if sulphides are present 5 cc. nitric acid are added) and about 20 cc. of hydrofluoric acid and the mixture evaporated to small volume on the steam bath and then to sulphuric acid fumes on the hot plate or over a direct flame. (Hood.) Upon cooling, a little dilute hydrochloric acid is added and the mixture warmed. The solution is diluted with distilled water and filtered if any insoluble residue remains.

If a residue remains, the paper and residue are ignited in a platinum dish, about 2 grams of acid potassium sulphate added and the material fused to a clear melt. This fusion may be conducted in a flask, if desired. In the latter case rotate the flask during cooling to spread the melt over its sides. The fusion is now dissolved by adding about 25 cc. of water, a few drops of sulphuric acid and gently heating. All the alumina and iron will be in solution. Lead and barium, if present, will remain insoluble as sulphates and should be filtered off. The filtrate is added to the main solution.

*Removal of the Hydrogen Sulphide Group.* — (Omit if these elements are known to be absent.) The free acid is neutralized with ammonia (iron and alumina just clouding the solution). Hydrochloric acid is now added till the precipitate just dissolves and 5 cc. excess added. The solution is diluted to 300 cc. and $H_2S$ passed in until the solution is thoroughly saturated, 15 minutes of gassing should be sufficient. The precipitate is filtered off and washed with hydrogen sulphide water (a few drops of HCl being added to the water).

Hydrogen sulphide is expelled from the filtrate by boiling. If iron and alumina are to be determined together, nitric acid is now added in sufficient amount to oxidize the iron, the solution turning yellow. In the absence of chromium, titanium, uranium, glucinum, and phosphates (for separation from these, see Notes), proceed as follows:

2. Add to the solution 10 cc. of 10% ammonium chloride and 5 cc. conc. nitric acid. Dilute to about 150 to 200 cc. and heat to boiling.

3. Cool slightly, add carbonate-free ammonium hydroxide slowly from a burette until a slight permanent precipitate forms, and then drop by drop until the solution reacts alkaline to litmus paper and the odor of ammonia is faintly perceptible.

4. Allow the precipitate to coagulate, keeping the solution warm (water bath or steam plate) for 4–5 minutes. Add a few more drops of ammonia and heat nearly to boiling but do not boil. (See Notes.)

5. Filter the hot solution through an 11 c.m. filter, transferring as little as possible of the precipitate to the filter. Wash three or four times by decantation, as it is difficult to wash the gelatinous compound on the filter. Now transfer to the filter and wash two or three times, using hot water. The wash water should contain a little ammonium nitrate solution. See Reagents.

6. The gelatinous precipitate of aluminum hydroxide is apt to absorb or occlude other substances if present in the solution. Unless these are known to be absent, dissolve the precipitate by placing the filter and its contents in a beaker. Add 20 to 50 cc. of strong HCl. Heat gently, breaking up the filter by stirring with a rod. The paper pulp assists in subsequent washing, and does no harm in the final ignition. Dilute with an equal volume of water and then add ammonia in slight excess. Boil gently for 2 or 3 minutes. Transfer

the hydrate and pulp to a filter and wash again with hot water (containing $NH_4NO_3$) four or five times.

NOTE. If much manganese is present a repetition of the above procedure is recommended. The third precipitation eliminates appreciable quantities of impurities commonly carried down by aluminum hydrate. Allowance for the ash in the three filters should be made. This seldom exceeds 0.0004 gram per filter.

7. Pinch the top of the filter paper together and place in a weighed crucible, with the apex of the filter pointing up.

8. Place the crucible over a hot plate for 4–5 minutes, or in a sand bath iron dish placed over a free flame. Then place the crucible over a free flame until the filter paper is consumed.

9. Cover the crucible to prevent mechanical loss, and ignite strongly over a Meker blast lamp or in an electric oven (1800° F.) for about 30 minutes. Cool in a desiccator, then weigh.

10. Ignite again for about 5 minutes and again weigh. The alumina must be ignited until its weight is constant. Water is held tenaciously by the compound, but a thirty minute ignition over a Meker burner or good blast lamp or in an oven at bright red heat is sufficient to completely dehydrate the $Al_2O_3$.

11. The residue is usually reported as $Al_2O_3$. If preferred it may be calculated to aluminum by multiplying by 0.5303 or to a compound of aluminum by using the appropriate conversion factor.

## NOTES

**Separation from Iron.** Aluminum hydroxide is precipitated by the addition of sodium thiosulphate to its neutral or slightly acid solution, followed by sufficient $NH_4OH$ to make the solution slightly ammoniacal. Iron remains in solution.

**Phosphoric Acid.** In presence of phosphoric acid, the phosphates of iron and alumina together with the phosphates of the other elements of the group and those of the alkaline earths will be precipitated upon making the solution alkaline with ammonia. Should iron and alumina be the only elements of these two groups present in the solution, they may be precipitated together as phosphates, iron determined by titration and calculated to the phosphate salt, and alumina obtained by difference. Occasionally, however, it it necessary to remove phosphoric acid.

**Removal of Phosphoric Acid.** The material is fused with about six times its weight of a mixture of 4 parts $Na_2CO_3$ and 1 part $SiO_2$ (silex), and the melt extracted with water containing ammonium carbonate. Iron and aluminum remain on the filter, upon filtration, while sodium phosphate passes into solution. Both the precipitate and filtrate contain silica. The precipitate of iron and alumina is dissolved in hydrochloric acid and taken to dryness, the residue dehydrated as usual, then treated with dilute hydrochloric acid and silica filtered off. The solution contains iron and aluminum in form of chlorides.

**Separation of Aluminum from Chromium.** The solution is made strongly alkaline with sodium or potassium hydroxides and chromium oxidized by passing in chlorine gas or by adding bromine. The solution is now acidified with nitric acid and aluminum hydroxide precipitated by addition of ammonium hydroxide, chromium remaining in solution as a chromate.

Instead of the hydroxides and the halogen treatment oxidation of the chromium may be accomplished by adding sodium peroxide until the solution is strongly basic. The solution is boiled to decompose the excess of peroxide and then acidified.

**Separation of Aluminum from Manganese, Cobalt, Nickel, Zinc, the Alkaline Earths, and Alkalies.** Alumina may be precipitated with iron as the basic acetate free from Mn, Co, Ni, Zn, etc. (see page 370), or it may be thrown out as phosphate, see page 83.

In absence of phosphates, these elements do not interfere in the determination of aluminum by precipitation as the hydroxide, provided a double or treble precipitation is made as given in step 6 above.

**Separation of Aluminum from Titanium.** Details of the procedure are given under "Titanium."

**Separation of Aluminum from Uranium.** Aluminum is precipitated as a carbonate in presence of a large amount of ammonium salts by addition of a large excess of ammonium carbonate and ammonium sulphide, while uranium remains in solution as the complex compound $UO_3(CO_3)_3(NH_4)_4$.

**Separation from Glucinum.** Aluminum is soluble in the fixed alkalies and remains in solution on boiling; glucinum also dissolves, but is precipitated on boiling. Glucinum is soluble in an excess of ammonium carbonate, aluminum is not.

For additional separations see chapter on element in question.

Ammonia should be free from carbonates. Upon long standing with frequent exposure to air the ammonia takes up $CO_2$, forming carbonate of ammonia. Freshly distilled ammonia will be pure, the carbonate being precipitated by addition of lime in the distilling flask. Ammonia is best kept in a ceresine or paraffine bottle. It will then remain free from silica, which it invariably contains when confined in glass bottles.

**Long heating** of the mixture containing the aluminum precipitate is objectionable.

1. The solution is apt to become acid owing to the decomposition of ammonium salts and the volatilization of ammonia.

2. The precipitate will become slimy and will be difficult to wash and filter. It is preferable to redissolve and again precipitate if this condition occurs.

3. The $CO_2$ of the air is apt to be absorbed by the solution, causing the precipitation of calcium carbonate, etc., should the solution be exposed for any length of time.

4. Silica from the beaker will contaminate the precipitate.

Hence it is advisable to filter as soon as possible after making the precipitation of $Al(OH)_3$.

**Washing the precipitate with ammonium nitrate** prevents the aluminum from passing through the filter and keeps it from packing. It favors the formation of the insoluble hydrogel form of the hydrate while preventing the formation of the soluble hydrosol. Ammonium chloride may be used in place of nitrate.[1]

Aluminum hydroxide is soluble in acids and alkalies. The ignited oxide, $Al_2O_3$, is insoluble in acetic acid but is soluble in mineral acids and the fixed alkalies. It is rendered very difficultly soluble in acids by strong ignition, generally requiring fusion with sodium carbonate or potassium bisulphate with subsequent acid treatment to effect solution.

$Al_2O_3$, *m.w.*, 102.2: *sp.gr.*, 3.73 to 3.99; *m.p.*, 2020° C.

A yellow or reddish precipitate indicates the presence of iron, an element frequently present with aluminum. Should this be the case, iron must be determined, either in a separate portion of the sample, or in the residue obtained by the procedure outlined. The amount of $Fe_2O_3$ is subtracted from the total residue, and $Al_2O_3$ obtained by difference.

[1] W. Blum, Jour. Am. Chem. Soc., **38,** 7, 1282, 1916. C. F. Sidener and Earl Pettijohn, Jour. Ind. Eng. Chem., **8,** 8, 714, Aug., 1916.

If **phosphoric acid** is present the phosphate of alumina will precipitate together with the phosphates of elements insoluble in alkaline solutions. Should phosphoric acid be present either its removal is essential, or the phosphate method for alumina should be followed.

**Fluorides** hinder the precipitation of aluminum.[1] Evaporation to dryness and heating the residue to redness will transform fluorides to oxides and overcome this difficulty.

**Sulphates** tend to hold up aluminum from precipitation and a certain amount of sulphuric acid is occluded by the aluminum hydroxide precipitate. Magnesium is more apt to precipitate with alumina in presence of sulphates. Ammonium chloride greatly lessens this difficulty.

**Traces of alumina** may be recovered from the filtrate by evaporation to dryness, ignition and resolution with HCl. The $Al(OH)_3$ is now precipitated with $NH_4OH$.

Since alumina absorbs moisture from the air, the crucible containing this compound should be kept covered in a desiccator until weighed.

Ammonium hydroxide, in presence of sufficient $NH_4Cl$, will not precipitate $Mg(OH)_2$ since the addition of $NH_4Cl$ increases the ammonium ions in the solution and, by the common ion effect, represses the hydroxyl ions of the base, $NH_4OH$, so that there are insufficient hydroxyl ions for the solubility product of $Mg(OH)_2$ to be exceeded; therefore magnesium remains in solution. A discussion of the theory of solubility product and law of mass action may be found in the author's work on Qualitative Chemical Analysis, published by D. Van Nostrand Company. Reference is also made to Vol. I of The Elements of Qualitative Chemical Analysis, by Julius Stieglitz, published by the Century Company.

[1] E. P. Veitch, Jour. Am. Chem. Soc., **22,** 246, 1900. W. R. Bloor, ibid., **29,** 1603, 1907. L. P. Curtman and H. Dubin, ibid., **34,** 1485, 1912.

## PRECIPITATION OF ALUMINUM AS A PHOSPHATE

**Principle.** — This procedure, developed by Carnot,[1] is of special value in determination of aluminum in presence of iron. It is founded on the reaction that aluminum is precipitated as the neutral phosphate, from a boiling solution faintly acid with acetic acid. Iron, reduced to the ferrous condition by addition of sodium thiosulphate, $Na_2S_2O_3$, does not interfere.

**Procedure.** — *Solution of the Sample.* A sample of 10 grams of iron or steel, in a platinum dish, covered with a piece of platinum foil, is dissolved by addition of hydrochloric acid. The solution is diluted to about 100 cc. and filtered into a flask, the residue of carbon, silica, etc., is washed thoroughly and the filtrate is neutralized by addition of ammonium hydroxide and ammonium carbonate; no permanent precipitate should form.

**Precipitation of Aluminum Phosphate.** — A little sodium thiosulphate is added, and when the liquid, at first violet, becomes colorless, 2 or 3 cc. of a saturated solution of sodium phosphate and 5 or 6 grams of sodium acetate, dissolved in a little water, are added. The solution is boiled until free of sulphurous acid odor (about three-quarters of an hour). The solution is filtered off from the precipitated aluminum phosphate (mixed with a little silica and ferric phosphate) and washed with boiling water.

**Purification of Aluminum Phosphate.** — The precipitate on the filter is treated with hot dilute hydrochloric acid, the filtrate caught in a platinum dish, and then evaporated to dryness and heated at 110° C. for an hour to dehydrate silica. The residue is taken up with dilute hydrochloric acid and the solution filtered free of silica. Upon dilution to about 100 cc. with cold water, the solution is neutralized as before, a little thiosulphate is added to the cold solution and then a mixture of 2 grams of sodium thiosulphate and 2 grams of sodium acetate.

The material is boiled for half an hour or more, filtered, and the aluminum phosphate residue washed with hot water, then dried, ignited and weighed as aluminum phosphate. The residue contains 22.19% Al.

$$AlPO_4 \times 0.2219 = Al. \quad AlPO_4 \times 0.4185 = Al_2O_3.$$

NOTE. Properties of $AlPO_4$, *m. w.*, 122.14; *sp. gr.*, 2.59; infusible, insoluble, in $H_2O$ and in $HC_2H_3O_2$, soluble in mineral acids and in alkalies; white, amorphous salt.

[1] A. Carnot, Moniteur Scientifique, 1891, p. 14.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### COLORIMETRIC ESTIMATION OF MINUTE AMOUNTS OF ALUMINUM WITH ALIZARIN S. — ATACK'S METHOD[1]

**Reagent.** — 0.1% alizarin S.

**Procedure.** — The original solution (5 to 20 cc.) is acidified with hydrochloric or sulphuric acid. Ten cc. of glycerin and 5 cc. of a 0.1% solution of alizarin S are added, the solution made up to about 40 cc. with water (in presence of much iron or chromium, citric acid is added to form the double citrates) and then rendered slightly ammoniacal. After standing for five minutes, the cold solution is acidified with dilute acetic acid, the alizarin S acting as indicator (red coloration) until no further change in the coloration occurs. The liquid is then made up to 50 cc. and compared with a standard. Suitable amounts of aluminum for estimation are 0.005 to 0.05 milligrams, the solution under examination being suitably diluted if necessary.

BAUXITE ANALYSIS[2]

| Characteristic bauxites... | $H_2O$ | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | $TiO_2$ |
|---|---|---|---|---|---|
| Arkansas..... | | 6.4% | 1.43% | 87.3% | 3.99% |
| Georgia..... | 36% | 9–15 | 1–14 | 42–62 | 1.8–2.3 |
| Tennessee..... | 27.6 | 18.4 | 4.1 | 49.9 | |

**Sampling.** — The bauxite received in cars is sampled during the unloading according to the standard procedure for ores. If the sample is a composite aliquot parts of the total weights are taken and mixed, e.g., suppose three cars contained respectively 23,000, 32,500, and 26,340 pounds, then the aliquots would be 23, 32.5 and 26.34 pounds, which mixed, would make a representative sample of the shipment. The ore is broken down, quartered, ground down and again quartered. The moisture is determined on 1000 grams, dried in the oven at 100° C. for one hour, the sample being spread out on a sheet of manilla paper. The dried sample is placed in a large bottle for analysis.

**Extraction of Ores of Aluminum for Their Commercial Valuation.** — Twenty-five grams of bauxite, alunite or clay, placed in a 600 cc. Kjeldahl flask with reflux condenser are digested for one hour with 60 cc. 10 N (48%) sulphuric acid. Time being taken when the mix begins to boil. The flame is so regulated that the water drips back into the flask from the condenser at the rate of 12 to 15 drops per minute. When the digestion is completed 150 cc. of hot water are introduced through the condenser. The mixture is now filtered using a Büchner funnel and suction. The residue is washed with six 100 cc.

[1] F. W. Atack, Jour. Soc. Chem. Ind.; **34,** 936 (1915); C. A. **9;** 23; 3186 (1915).

[2] Bauxite and kaolin are two sources of alumina of commercial importance. The alumina of certain grades of clay is made available for acid extraction by roasting at a definite temperature.

portions of water and the filtrate made up to 1000 cc. A 200 cc. aliquot is made up to 1000 cc. and 100 cc. of this taken for determination of alumina as stated on next page.

**Insoluble Residue.** — The residue on the filter paper is ignited in a platinum dish over a low flame until the paper chars, and then over a good Meker blast for 15 to 20 minutes. Residue $\times$ 4 = per cent insoluble residue.

**Soluble Alumina.** — 100 cc. of the above solution (0.5 g.) is diluted with an equal volume of water, 10 cc. of hydrochloric and 2 cc. of nitric acids added and the solution boiled. Iron and alumina are now determined.

**Soluble Iron.** — 200 cc. of the solution (1.0 g.) is oxidized by adding a few crystals of potassium chlorate and the solution taken to dryness. The residue is taken up with 10 to 15 cc. of concentrated hydrochloric acid and again evaporated to dryness to expel chlorine, then taken up with 25 cc. of hydrochloric acid and the iron determined by titration. The stannous chloride method is used for samples containing less than 5% iron and the dichromate method for ores containing over 5%.

**Silica.** — 1 gram of the dried bauxite is digested in 90 cc. of an acid mixture containing 12 parts of dilute sulphuric acid, 1 : 3, together with 6 parts of strong hydrochloric acid and 2 parts of nitric by volume, to this are added 10 cc. of sulphuric acid. The mixture is heated until fumes are evolved, then diluted with water and filtered. The residue is ignited and the ash fused with potassium bisulphate. The cooled fusion is taken up with 5 cc. sulphuric acid and 20 cc. of water and digested until only a white residue remains. This filtered off, washed and ignited = $SiO_2$.

**Titanium Oxide.** — This is best determined colorimetrically on a 0.1 gram sample according to the procedure outlined in the chapter on Titanium.

**Iron and Alumina.** — These are determined by the usual procedure: — oxidation with potassium chlorate, precipitation with ammonium hydroxide and ignition. Iron may be determined in a separate sample (100 cc. = 0.5 g.) by titration. $Al_2O_3$ = difference between weighed oxides and $Fe_2O_3$, after subtracting $TiO_2$ if present.

## VOLUMETRIC DETERMINATION OF AVAILABLE ALUMINA IN BAUXITE AND CLAYS [1]

This method is based on the solution of the sample in a known amount of sulphuric acid, and the titration of the excess acid with standard sodium hydroxide solution, and the alumina estimated from the amount of acid used to combine with it. It has been proven with long practice that this method is accurate within 0.5%, and is very satisfactory as a works control method. It is much more rapid than the regular gravimetric procedure.

Take a five gram sample that has been ground to pass through a 60-mesh sieve and put it into a 300 cc. Kjeldahl flask with about 28 to 30 grams of 40° Bé sulphuric acid, which is weighed from a weighing burette. (This acid may be measured with a burette and the weight calculated if so desired with a reasonable chance of error introduced.) Digest this at a gentle boil for one hour, giving the flask an occasional shaking. Care must be taken that good condensation is effected, otherwise a loss in acid will give high results. After the digestion wash down the condenser and filter the insoluble residue off on a Büchner funnel with suction, washing the residue acid free. Make the filtrate up to 2000 cc. in a volumetric flask. To a 200 cc. aliquot add 20 cc. of KF reagent, and 1 cc. phenolphthalein indicator and titrate to a permanent pink with standard N/10 NaOH.

**Reagents.**—The 40° acid must be made up very accurately and standardized against standard caustic.

1000 grams of potassium fluoride are dissolved in 1200 cc. of hot $CO_2$ free water, and then neutralized with HF or KOH as may be necessary, using phenolphthalein indicator. Filter this solution and dilute to 2000 cc. This solution should be kept in a wax-lined bottle.

Take 20 cc. of KF reagent and add 5 cc. of N/2 NaOH and one cc. of phenolphthalein indicator, and titrate with N/2 $H_2SO_4$. Apply this correction to the titration of the sample.

**Calculations:**

$$\frac{(\text{cc. N/10 } H_2SO_4 - \text{cc. N/10 NaOH}) \times .3473 \times 100}{\text{weight of sample}} = \% \; Al_2O_3 + Fe_2O_3$$

$\% \; Fe_2O_3 \times .64 = Fe_2O_3$ equivalent to $Al_2O_3$ which can be subtracted from the total oxides above, the result being the available alumina..

[1] By Harold E. Martin.

## ANALYSIS OF METALLIC ALUMINUM [1]

### Determination of Silicon

Acid Mixture: 400 cc. conc. nitric acid. 1200 cc. conc. hydrochloric acid. 600 cc. conc. sulphuric acid. 1800 cc. water.

**Fusion Method.** — Dissolve 1 gram of well mixed drillings in 35 cc. of acid mixture using a 4½-inch porcelain dish with a 5-inch cover glass. When the drillings are completely dissolved, evaporate the solution not only to fuming but to complete dryness, and bake. This insures the freedom of the solution from hydrochloric and nitric acids, and the complete dehydration of the silica. Take up the residue with 10 cc. of 25 per cent sulphuric acid and about 100 cc. of water; boil to complete solution of the sulphate, filter, wash well and ignite. Fuse the residue with eight to ten times its weight of sodium carbonate and take up the fused mass in a porcelain dish with sulphuric acid (1 : 1). Evaporate the resulting solution until copious fumes are evolved, which will cause the separation of the silica; dilute carefully, boil, filter, wash well and ignite in a platinum crucible and weigh. Treat the ash with hydrofluoric acid and a few drops of sulphuric acid; carefully ignite and weigh. The difference in the two weights obtained above represents the silicon as silica.

Calculate the silica to silicon by the factor 0.4693.

### Graphitic Silicon

Aluminum, sometimes if not always, contains some silicon in the graphitic state; this graphitic silicon does not oxidize to $SiO_2$ on ignition and is not volatile with HF, which two characteristics distinguish it from amorphous silicon.

To determine graphitic silicon the mixture of Si and $SiO_2$ obtained as in the solution method is treated in a weighed platinum crucible with 2–3 drops of $H_2SO_4$ and 2–3 cc. of HF.

The brown residue of Si remaining is strongly ignited and weighed; the silicon remaining is that which was in the metal in the graphitic state.

### Determination of Iron

**Permanganate Method.** — Cool the filtrate obtained from solution of the sample in acid mixture and reduce the iron present by passing the solution through a Jones reductor. Titrate immediately with a

[1] Standard Method of Analysis of the Aluminum Company of America. By courtesy of Mr. E. Blough, Chief Chemist.

solution of potassium permanganate of such strength that 1 cc. equals 0.0010 gram iron.

In all cases the precautions given for use of the Jones reductor should be observed, and explicit directions given in the chapter on Iron carefully followed. A blank determination is made by carrying out a regular iron determination with the metal sample omitted. The amount of potassium permanganate required to give the blank a distinct color is subtracted from the amount required to give the same color to each reduced solution.

**Determination of Aluminum in Iron and Steel.** — See Phosphate method for determining aluminum.

## ANTIMONY [1]

**Sb, at.wt. 120.2; sp.gr. 6.62; m.p. 630° C.; b.p. 1440° C.; oxides, $Sb_2O_3$, $Sb_2O_4$, $Sb_2O_5$**

Antimony is determined in the evaluation of its ores, in the analysis of drosses from the softening of lead, in alloys, notably type metal, bearing or antifriction metals, pewter, hardened lead alloys etc. It is generally required in the complete analysis of minerals of nickel, lead, copper, silver, in which antimony generally occurs as a sulphide. It is determined in the analysis of certain mordants, antimony salts, paint pigments, vulcanized rubber etc. It is looked for as an undesirable impurity in certain food products.

### OCCURRENCE

The element occurs free and combined in nature.

*Minerals* — *Native Antimony* frequently alloyed with arsenic, iron or silver, is a brittle tin-white metal with fine granular, steel-like texture, or is lamellar or radiated; opaque; metallic lustre; streak tin-white; hardness 3–3.5. It fuses easily, giving off white fumes; it colors the flame pale green.

*Stibnite*, $Sb_2S_3$ — a lead-gray mineral of bright metallic lustre, or may be black or with iridescent tarnish; imperfectly crystallized long, needle-shaped crystals, or granular to compact masses; opaque; brittle; lead-gray streak; hardness 2; fuses readily. This is the chief source of antimony.

Other minerals — *Kermesite* (red antimony), $Sb_2S_2O$; *Valentinite*, $Sb_2O_3$; *Allemonite*, $SbAs_3$; *Zinkenite*, $PbS.Sb_2S_3$. *Jamesonite*, $Pb_2Sb_2S_5$. *Bournonite*, $PbCuSbS_3$.

### DETECTION

The powdered mineral or alloy is dissolved in hydrochloric acid of aqua regia as the case may require. The following tests may be made on portions of the solution.

The solution is made decidedly alkaline with sodium hydroxide and saturated with hydrogen sulphide. The precipitate is filtered off and the solution made acid with hydrochloric acid — a red colored precipitate indicates antimony; arsenic and tin also, will precipitate. The sulphides are dissolved in strong hydrochloric acid, and heated to expel $H_2S$. The extract is diluted with water, and a rod of zinc and a platinum foil in contact with each other are placed in the solution. If the platinum becomes coated with a dark film, antimony is present.

[1] Suggestions for experimental work are given on page 90.

**Hydrogen Sulphide** precipitates the orange-colored sulphide of antimony from fairly strong hydrochloric acid solutions (1 : 4) in which several members of the group remain dissolved. Arsenic is also precipitated. The latter may be removed by boiling the solution containing the trichloride, $AsCl_3$ being volatile.

If antimony is already present as a sulphide, together with other elements of the hydrogen sulphide group, it may be dissolved out by treating the precipitate with sodium hydroxide, or potassium hydroxide, or sodium sulphide, or ammonium polysulphide. Antimony sulphide is reprecipitated upon acidifying the filtrate. Arsenic and tin will also be precipitated with antimony if they are present in the original precipitate. Should a separation be necessary, the precipitate is dissolved with hot concentrated hydrochloric acid, with the addition of crystals of potassium chlorate, from time to time, until the sulphides dissolve. The solution is placed in a Marsh apparatus, pure zinc added and the evolved gases passed into a neutral solution of silver nitrate. The black precipitate of silver antimonide and metallic silver are filtered off, washed free of arsenous acid, and the antimonide dissolved in strong hydrochloric acid (silver remains insoluble). The orange-colored antimony sulphide may now be precipitated by diluting the solution with water and passing in $H_2S$ gas to saturation.

**Minerals** which contain antimony, when heated alone or with 3 to 4 parts of fusion mixture ($K_2CO_3$ and $Na_2CO_3$) on charcoal, yield dense white fumes, a portion of the oxide remaining as a white incrustation on the charcoal. A drop of ammonium sulphide placed upon this sublimate gives a deep orange stain.

**Hydrolysis.** — Most of the inorganic antimony salts are decomposed by water, forming insoluble basic salts, which in turn break down to the oxide of antimony and free acid. An excess of tartaric acid prevents this precipitation.

**Traces of Antimony.** — Nascent hydrogen liberated by the action of zinc and hydrochloric or sulphuric acid reacts upon antimony compounds with the formation of stibine. This gas produces a black stain on mercuric chloride or silver nitrate paper. Details of the procedure are given under the quantitative method for determining minute amounts of antimony.

### Distinction between Antimonous and Antimonic Salts

*Chromates* form with antimonous salts green chromic salts and antimonic salts.

*Potassium Iodide* reduces antimonic salts, free iodine being liberated.

## SUGGESTIONS FOR EXPERIMENTAL WORK

For experience in the determination of antimony the student is advised to start with the determination of antimony in alloys as given on page 93. Following this determine antimony in an ore according to the method given on page 91.

## GRAVIMETRIC METHODS FOR THE DETERMINATION OF ANTIMONY

The accuracy and rapidity of volumetric methods for the determination of antimony leave little to be desired in the estimation of this element, so that the more tedious gravimetric methods are less frequently used and will not be included here.

## VOLUMETRIC METHODS FOR THE DETERMINATION OF ANTIMONY

### DETERMINATION OF ANTIMONY IN ORES — PERMANGANATE METHOD

**Preparation and Solution of the Sample.** — In dissolving the substance containing antimony it must be remembered that metallic antimony is practically insoluble in cold dilute hydrochloric, nitric or sulphuric acid and the oxides, $Sb_2O_3$ or $Sb_2O_5$, are precipitated in strong nitric acid. The element, however, is readily soluble in hydrochloric acid containing an oxidizing agent, such as nitric acid, potassium chlorate, chlorine, bromine, etc. The oxides of antimony are soluble in hydrochloric acid and the caustic alkalies. The procedure for decomposition of ores is as follows:

Half a gram to 1 gram of the finely ground ore, placed in the pear shaped " Low's " flask is decomposed as follows:

Add 5 grams of acid potassium sulphate, $\frac{1}{3}$ of a 20 cc. crucible full (free from chlorides), 5 cc. of sulphuric acid and a small piece of filter paper (this furnishes carbon for reduction of arsenic and antimony), and heat over a direct flame until the solution becomes clear and a pale straw color. Tilt the flask at an angle of 30 degrees and expel the greater part of the acid. The flask may be held by a special holder or crucible tongs and manipulated over the flame. Remove from the flame and rotate the flask allowing the melt to cool on the sides of the flask.

**Removal of Arsenic.** — To the cold melt add 25 cc. of water and warm gently until the cake breaks up, then add 50 cc. of strong hydrochloric acid, and allow to stand a few minutes until the material dissolves, shaking the mixture to assist solution.

Pass in $H_2S$ gas in a rapid stream until the solution is saturated and all the arsenic has precipitated. The precipitate should appear yellow. An orange color indicates antimony which precipitates if insufficient HCl is present. The antimony remains in solution. About 10 to 15 minutes should be sufficient. During the gassing prepare a Witt plate filter with an inch and a quarter perforated plate in a funnel covered by a filter, wet into position, with sufficient paper pulp to prevent leakage of precipitate. The funnel should be a

long stem funnel, preferably with loop tube. Moisten the filter with 2 : 1 HCl solution.

Now carefully pour the contents of the flask on the filter, avoiding stirring up the paper pulp, and catching the filtrate in a 500 cc. beaker. Wash the flask and delivery tube with 2 : 1 HCl solution, pouring the solution on the arsenic sulphide; repeat this seven times with the cold HCl mixture. Note the volume of the acid mixture containing the antimony chloride by placing a mark on the beaker receiving the filtrate. (Arsenic may be determined in the precipitate $As_2S_3$.)

Dilute the acid extract with twice its volume using hot water, antimony sulphide will precipitate. Saturate the solution with $H_2S$ to completely precipitate the antimony, and filter through an 11 cm. filter. Wash the precipitate six times or more to remove chlorides, using $H_2S$ water, acidulated with 2–3 drops of sulphuric acid.

Place a clean "Low's" flask under the funnel. Punch a hole through the filter and wash the greater part of the sulphide into the flask, using as little water as possible. Dissolve off the adhering sulphide from the delivery tube and filter with a 5% solution of sodium hydroxide, catching the alkali solution in the flask containing the antimony. Use just a sufficient amount to dissolve all of the sulphide.

Add to the solution about 3 grams ($\frac{1}{4}$ of a 20 cc. crucible) of anhydrous sodium sulphate and 10 cc. of strong sulphuric acid. Boil down to small bulk over a free flame. By means of a holder manipulate the flask over the flame until the mass is reduced to a melt. Allow to cool rotating the flask to spread the melt over its sides.

To the cold residue add 50 cc. of water and 10 cc. of strong HCl. Heat to boiling to expel $SO_2$. Add 10 cc. more of HCl, cool under tap, dilute to 150 cc. with cold water and titrate with standard potassium permanganate to a faint pink color.

Antimony is oxidized from $Sb^{iii}$ to $Sb^{v}$ ($Sb_2 \Rightarrow 2\ O$) hence a 0.1 N solution is equivalent to 0.006 gram Sb, or the Fe value of the $KMnO_4$ multiplied by 1.076 = the Sb value.

Note. Under the conditions of acidity antimony is precipitated free from interfering elements.

**Separation of Antimony from Tin.** — Upon the removal of arsenic, antimony may be determined directly in the presence of tin by one of the volumetric methods given later. If a gravimetric separation is desired, it may be made according to a modification of Clark's method, which depends upon the fact that antimony is completely precipitated from a solution containing oxalic acid by hydrogen sulphide, whereas tin is not. The tin must be in the stannic form, otherwise the insoluble crystalline stannous oxalate will form.

## ANTIMONY IN ALLOYS

### POTASSIUM BROMATE METHOD FOR DETERMINING ANTIMONY

**Outline.** — This method is of special value in determining antimony in hard lead and alloys. The process is based upon the oxidation of antimony from the trivalent to the pentavalent form by potassium bromate, the following reaction taking place:

$$KBrO_3 + 3SbCl_3 + 6HCl = 3SbCl_5 + KBr + 3H_2O.$$

#### Standard Solutions

*Antimony Chloride Solution.* Six grams of the C.P. pulverized metal are dissolved in 500 cc. of concentrated hydrochloric acid together with 100 cc. of saturated bromine solution, more acid and bromine added if necessary to effect solution. After expelling the bromine by boiling, about 200 cc. of concentrated hydrochloric acid are added and the whole made up to one liter. Fifty cc. = 0.3 gram antimony.

*N/10 Potassium Bromate Solution.* 2.82 grams of C.P. salt are dissolved in water and made up to 1 liter. Theoretically 2.7852 grams are required, but the salt invariably contains potassium bromide as an impurity. The solution is standardized against 50 cc. of the antimony chloride solution, which has been reduced with sodium sulphite according to the standard scheme. One cc. of N/10 $KBrO_3$ = 0.006 gram Sb.

*Methyl Orange.* 0.1 gram M. O. per 100 cc. of distilled water.

*Saturated Bromine Solution.* Hydrochloric acid saturated with bromine.

**Procedure.** *Solution.* One gram of the finely divided alloy is brushed into a 500 cc. beaker, 100 cc. of concentrated hydrochloric acid and 20 cc. of saturated bromine solution are added. The beaker is covered and placed on the steam bath until the metal dissolves. It may be necessary to add more bromine and acid to effect complete solution. In case the oxides of antimony and tin separate out and do not redissolve, fusion with sodium hydroxide may be necessary. Bromine is now expelled by boiling down to about 40 cc.

*Reduction.* One hundred cc. of concentrated hydrochloric acid and 10 cc. of a fresh saturated solution of $Na_2SO_3$ are added and the solution boiled down to 40 cc., on a sand bath, to expel arsenic and the excess of normal sodium sulphite. Samples high in arsenic may require a repetition of the reduction.

*Titration.* The cover and sides of the beaker are rinsed down with 20 cc. of hydrochloric acid (sp. gr. 1.2) followed by a few cc. of hot water and the solution heated to boiling on a sand bath. The standard bromate solution is now run into the hot solution of antimony to

within 2 to 3 cc. of the end point, this having been determined in a preliminary run with methyl orange added in the beginning, 4 drops of methyl orange are added and the titration completed cautiously until the color of the indicator is destroyed. If iron or copper is present the final product will appear yellow. Since the end-reaction is slow the last portion of the reagent should be added drop by drop with constant stirring.

1 cc. N/10 $KBrO_3$ = 0.006 gram Sb.

Notes. Since antimony chloride begins to volatilize at 195° C. and boils at 220° C. it is advisable not to carry the concentration too far while expelling arsenic.

Lead, copper, zinc, tin, silver, chromium, and sulphuric acid have no effect upon the determination, but large quantities of calcium, magnesium, and ammonium salts tend to make the results high. Low found that copper produced high results, approximately .012 % too high for every 0.1 % of copper present. The author (W.W.S.) finds, however, that with the procedure given above, amounts of copper as high as 15 % produced no difficulty beyond a yellow coloration of the solution. With larger amounts of copper, the end-point became difficult to detect owing to the depth of this yellow color, so that in case of brass and copper alloys, the method must be modified by a procedure for removal of the copper. Lead up to 95 % caused no difficulty. Iron, in amounts such as are commonly met in alloys of lead, does not interfere.

During the course of analysis antimony may be isolated as the sulphide; this is dissolved in strong hydrochloric acid, and reduced and concentrated to expel arsenic that may be present as a contamination, and the resulting solution titrated with potassium bromate as directed above.

Sources of Error. (*a*) Imperfect volatilization of arsenic. (*b*) Incomplete expulsion of $SO_2$. (*c*) Over-titration if insufficient hydrochloric acid is present.

No loss of antimony occurs at temperatures below 120° C.

**Potassium Iodide Method for Antimony.** See Standard Methods of Chemical Analysis by W. W. Scott.

## DETERMINATION OF ANTIMONY BY OXIDATION WITH IODINE

The procedure originated by Mohr and modified by Clark, depends upon the reaction $Sb_2O_3 + 2I_2 + 2H_2O = Sb_2O_5 + 4HI$.

The reaction takes place when iodine is added to a solution of antimonous salt in presence of an excess of alkali bicarbonate. In an acid solution oxidation with iodine does not go beyond $Sb_2O_3$. The method is useful for determining antimony in alloys.

### Antimony in Solder Metal and Alloys with Tin and Lead

1. **Procedure.** — Dissolve 2 grams of the sample of alloy in concentrated hydrochloric acid.

2. When the metal is all in solution, add crystals of iodine until the solution is thoroughly permeated. The color at this point should be a deep purple.

3. Boil until all of the iodine fumes have been driven out. The metallic antimony which did not go into solution in the hydrochloric acid should now be all dissolved. If it is not, add more iodine until the solution is complete.

4. When all is in solution and the color changes to a straw yellow, cool, add a few cc. of starch solution. If a blue color appears, due to an excess of iodine, run in N/10 sodium thiosulphate solution until colorless. In case there is no blue color developed, add N/10 iodine until a faint blue appears.

5. Now add 50 cc. of a saturated solution of Rochelle salts. Make alkaline to litmus by adding 25% sodium hydrate solution. Then make slightly acid with HCl and finally alkaline with sodium bicarbonate.

6. Cool and titrate with N/10 iodine.

1 cc. N/10 I = 0.006 g. Sb.

NOTE. "The method gives very good results. I have checked it up when there was one-tenth of a gram of known antimony present and the results were within a reasonable limit of accuracy." [1]

[1] Method communicated to author by Mr. B. S. Clark.

## DETERMINATION OF SMALL AMOUNTS OF ANTIMONY

**Outline of the Method. Preparation of Standard Stains.** — Extreme care must be taken when preparing the standard stains.

Wash the generator, see Fig. 43, thoroughly with distilled water, place freshly prepared lead acetate cotton in the bulb, *B*, No. 2, and see that the top of part *F*, No. 2, is exactly $\frac{5}{16}''$ from the top of part *A*, No. 2.

Now introduce into bottle of generator, No. 3, the required amount of antimony as desired and then add 50 cc. redistilled HCl, As free, 2 cc. stannous chloride solution and make up to 220 cc. with distilled water.

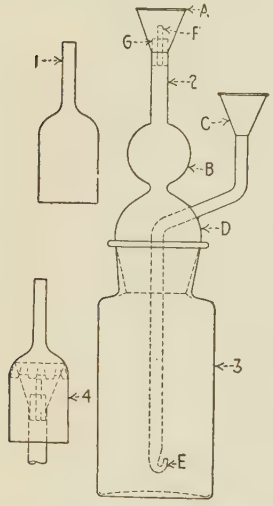



Fig. 43. Fitzpatrick Apparatus for Determining Traces of Antimony.

The disc of mercuric chloride test paper is now placed on top of funnel *A*, No. 2, and the glass cap, No. 4, is forced over the paper holding it in place.

Now introduce 15 gms. metallic zinc shot and place the No. 2 section with No. 1 attached into the No. 3 or bottle of generator. The apparatus now being assembled, observe that the apparatus is fitted together tightly, because as soon as the zinc is introduced, Stibine, $SbH_3$, is generated immediately. Place the generator into the water bath to maintain constant temperature which should be about 70° F. Allow the generator to operate for 1 hour.

The glass cap, No. 1, is now removed and the test paper is developed in a small beaker with 5% $NH_4OH$ solution for three minutes, then washed 5 times with distilled water. The test paper is now toned with a 1% $AuCl_3$ solution by allowing the test paper to remain in solution for five minutes. The test paper will now have a violet or purple stain, the intensity depending on the amount of antimony introduced. Wash the paper 5 times with distilled water and preserve in 50 cc. glass stoppered bottles containing about 5 cc. water. Keep bottles in dark place, because the stains darken on exposure to light.

Duplicate tests are made, with a hydrochloric acid solution of the sample examined, according to the procedure outlined for the preparation of the standard stains (omitting the addition of antimony). The stains are compared with the standard stains and the amount of antimony thus determined. Arsenic should be absent. If present in the sample it must be removed by distillation. See chapter on Arsenic.

For further details consult Standard Methods of Chemical Analysis by W. W. Scott, D. Van Nostrand Co., N. Y.

## ARSENIC

| | | | | |
|---|---|---|---|---|
| | cryst. | 5.73 | 850° C. | subl. 554° C. |
| $As_4$ at.wt. 74.96 — | sp.gr. | m.p. | b.p. | |
| | amorp. | 4.72 | ... | <360° C. |

Oxides, $As_2O_3$, $As_2O_5$.[1]

The determination of arsenic is required in the valuation of native arsenic, white arsenic and other arsenic minerals. The element is estimated in the analysis of copper ores, in speiss, regulus, iron precipitates (basic arsenic), paint pigments, Scheel's green, in shot alloy and in many metals. It is estimated in germicides, disinfectants, and insecticides — Paris green, lead arsenate, zinc arsenite, etc. Traces of arsenic occur as undesirable impurities in food products.

### OCCURRENCE

Arsenic occurs free and combined in nature.

**Minerals.** — Among the minerals of arsenic the following are of special importance: — *Native Arsenic*, As. The element is frequently alloyed with antimony, bismuth, nickel, cobalt, iron, silver or gold. It is a tin-white metal, tarnishing almost black; opaque; brittle; granular fracture; tin-white streak; hardness 3.5. Heated it volatilizes with white fumes without fusion, coloring the flame pale blue.

*Realgar*, $As_2S_2$, a soft orange-red mineral, with resinous lustre; translucent to transparent; crystalline also massive; streak orange red; hardness 1.5–2.

*Orpiment*, $As_2S_3$, lemon-yellow mineral with resinous or pearly lustre; translucent to opaque; cleavage in plates or leaves, also granular masses; streak lemon-yellow; hardness 1.5–2.

*Arsenopyrite*, FeAsS, a silvery white to gray mineral with metallic lustre; compact or in granular masses; opaque; brittle; grayish-black streak; prismatic cleavage; hardness 5.5–6.

*White Arsenic*, $As_4O_6$, occurs native in fine hair-like crystals. Artificial in two forms — "glass" and "powder."

[1] **Suggestion for the Student.**—For practice use arsenious oxide and follow procedure on page 105.

## DETECTION

For obtaining a solution for the tests see page 99.

**Hydrogen sulphide** precipitates the yellow sulphide of arsenic, $As_2S_3$, when passed into its solution made strongly acid with hydrochloric acid. If the solution contains more than 25% hydrochloric acid, (sp.gr. 1.126) the other members of the hydrogen sulphide group do not interfere, as they are not precipitated from strong acid solutions by hydrogen sulphide. Arsenic sulphide is soluble in alkaline carbonates. (Antimony sulphide, $Sb_2S_3$, reddish yellow, is insoluble in alkaline carbonates.)

**Volatility of the chloride, $AsCl_3$,** is a means of separation and detection of arsenic. Details of the procedure are given on page 100.

**Traces of arsenic** may be detected by either the Gutzeit or Marsh test for arsenic. Directions for the Gutzeit test are given at the close of the volumetric procedures.

**Distinction between Arsenates and Arsenites.** — Magnesia mixture precipitates white, $MgNH_4AsO_4$, when added to ammoniacal solutions containing arsenates, but it produces no precipitate with arsenites.

Red silver arsenate and yellow silver arsenite are precipitated from neutral solutions by silver nitrate. An arsenate gives a yellow precipitate with ammonium molybdate solution.

**Comparison of the Marsh Tests for Antimony and Arsenic.** — Stibine and arsine are formed by the reduction of compounds of the corresponding elements by nascent hydrogen; both leave a deposit in the form of a black mirror on a cold white surface when the flames of the ignited gases impinge against the cold body. The stain of arsenic, however, is soluble in a hypochlorite solution, while that of antimony is not. Arsine passed through a solution of $AgNO_3$ will reduce the compound, forming black flakes of metallic silver. Stibine does not reduce silver nitrate, but precipitates black silver antimonide. The arsenic mirror, dissolved in a drop of $HNO_3$ then evaporated to dryness and the residue moistened with a drop of silver nitrate, gives a brick-red color. Antimony remains colorless. The spot dissolved in ammonium sulphide and evaporated to dryness yields a bright yellow residue. Antimony residue is orange-red. If arsine is conducted through a hard glass tube with a constriction, and this portion of the tube is heated, an arsenic mirror forms in advance of the flame. Stibine decomposes, depositing antimony immediately above the flame, since antimony is less volatile.

**Dry Tests.** — The powdered mineral placed on charcoal and heated with the reducing flame by means of a blowpipe gives an odor of garlic. The arsenic coats the charcoal with a white incrustation, which is volatile in the oxidizing flame.

The mineral containing arsenic held on a thread of asbestos in a reducing flame tinges the flame white and makes a black deposit on a cold body held in the flame. If the stain is carefully heated to 200° C. it acquires a silvery lustre.

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

**Procedures for Examination of Industrial Products Containing Arsenic.** — In dissolving arsenic compounds it will be recalled that the oxide, $As_2O_3$, is not readily acted upon by dilute acids — hydrochloric or sulphuric. The compound is soluble, however, in alkaline hydroxides and carbonates. Nitric acid oxidizes $As_2O_3$ to the higher oxide, $As_2O_5$, which is soluble in water. The sulphides $As_2S_3$ and $As_2S_5$ are practically insoluble in hydrochloric or sulphuric acids, but are dissolved by the fixed alkalies and alkali sulphides. All arsenites, with the exception of the alkali arsenites, require acids to effect solution.

**Pyrites Ore and Arseno-pyrites.** — The amount of the sample may vary from 1 to 20 grams, according to the arsenic content. The finely ground sample in a large casserole is oxidized by adding 10 to 50 cc. of bromine solution (75 cc. KBr + 50 cc. liquid Br + 450 cc. $H_2O$) covering and allowing to stand for fifteen minutes, then 20 to 50 cc. of strong nitric acid are added in three or four portions, allowing the action to subside upon each addition. The glass cover is raised by means of riders, and the sample evaporated to dryness on the steam bath; 10 to 25 cc. of hydrochloric acid are now added and the sample again taken to dryness. Again 10 to 25 cc. of hydrochloric acid are added and the sample taken to dryness. Finally 25 cc. of hydrochloric acid and 75 cc. of water are added, and the mixture digested over a low flame until all the gangue, except the silica, is dissolved. The solution is now examined for arsenic by distillation of the arsenic after reduction, the distillate being titrated with standard iodine solution according to directions given later.

**Arsenous Oxide.** — The sample may be dissolved in caustic soda, the solution neutralized with hydrochloric acid, and the resulting sample titrated with iodine.

**Fusion Method.** — One gram of the finely powdered mineral is fused in a nickel crucible with about 10 grams of a mixture of potassium carbonate and nitrate, 1:1, and the melt extracted with hot water. Two hundred cc. of a saturated solution of $SO_2$ is added to the filtrate to reduce the arsenic, the excess of $SO_2$ then expelled by boiling, the solution diluted with dilute sulphuric acid, and arsenic determined in the filtrate. (See also "Preliminary Considerations," page 100.)

**Arsenic in Sulphuric Acid.** — *Arsenous acid* may be titrated directly with iodine in a 20- to 50-gram sample, which has been diluted to 200 to 300 cc. with water and nearly neutralized with ammonium hydroxide and then an excess of sodium acid carbonate added, followed by the iodine titration.

**Lead Arsenate.** — Ten grams of the thoroughly mixed paste or 5 grams of the powder are dissolved by treating with 25 cc. of 10% hot sodium hydroxide solution, and diluted to 250 cc. An aliquot

part, 50 cc. (= 2 grams paste and 1 gram powder) is placed in an Erlenmeyer flask and 20 cc. of dilute sulphuric acid, 1:1, added, and the solution diluted to 150 cc. About 3 grams of solid potassium iodide are added and the solution boiled down to about 50 cc. (but not to fumes). The liquor will be colored yellow by free iodine. Tenth normal sodium thiosulphate is added drop by drop until the free iodine is neutralized (solution loses its yellow color); it is now diluted to about 250 cc. and the free acid neutralized by ammonium hydroxide (methyl orange indicator), then made slightly acid with dilute sulphuric acid, and an excess of bicarbonate of soda added. The arsenic is titrated with standard iodine.

The arsenic may be reduced by placing the 50-cc. sample in a Kjeldahl flask, adding 25 cc. of strong sulphuric acid (1.84 sp.gr.), $\frac{1}{2}$ gram tartaric acid and 2 grams acid potassium sulphate, $KHSO_4$, and digesting over a strong flame until the organic matter is destroyed and the solution is a pale yellow color. The cooled acid is diluted and neutralized, etc., as directed above.

**Preliminary Considerations.** — As in the case of antimony, the accuracy and rapidity of the volumetric methods for the determination of arsenic make these generally preferable to the more tedious gravimetric methods. Arsenic bearing ores may be brought into solution by decomposing in a pyrex glass flask (Low's flask) by fusion with sodium sulphate, adding 4 grams of the anhydrous salt and about 6 cc. sulphuric acid per 0.5 gram sample, and a small piece of filter paper to reduce the arsenic, conducting the fusion over a free flame until most of the free acid is expelled. The melt spread over the sides of the flask is cooled and brought into solution with water. Arsenic is now isolated either by distillation according to the method following or by precipitation as arsenic sulphide in a hydrochloric acid solution containing approximately 26 % free HCl (sp. gr. 1.135) or 2 parts HCl (sp. gr. 1.2) to 1 part of water. The other elements remain in solution in a hydrochloric acid solution of this strength.

### Isolation of Arsenic by Distillation as Arsenous Chloride

By this method arsenic may be separated from antimony, tin, and from other heavy metals. It is of special value in the direct determination of arsenic in iron ores, copper ores, and like products and has a wide application. The procedure depends upon the volatility of arsenous chloride at temperatures lower than the other heavy metals. In a current of HCl gas, arsenous chloride begins to volatilize below 108° C., and is actively volatile at 120° C.; antimony starts to volatilize at 125° C., but is not actively volatile until a temperature of 180° has been reached. The boiling-point of arsenous chloride, $AsCl_3$, is 130.2°; antimony trichloride, $SbCl_3$, is 223.5°; and that of stannous chloride, $SnCl_2$, is over 603°; other chlorides having still higher boiling-points. Tin in its higher form, $SnCl_4$, is readily volatile, boiling-point is 114° C., so that it is necessary to have it in its divalent form to effect a separation from arsenic. When heavy metals are present in the residue remaining from the arsenic distillate, or when zinc chloride is added to raise the boiling-point, antimony may also be separated by distillation by carrying the solution to near dryness, adding concentrated HCl by means of a separatory funnel, drop by drop, during further distillation of the concentrate. Arsenic passes into the first portions of the distillate.

Commercial hydrochloric acid invariably contains arsenic, so this must be purified by redistillation in presence of an oxidizing agent to oxidize the arsenic to the non-volatile arsenic pentachloride, $AsCl_5$, form, or by treatment with $H_2S$ and filtration. A blank run should be made on the reagents used, especially when traces of arsenic are to be determined.

**Procedure.** — If arsenic is present as arsenic chloride, as prepared in the method for solution of iron ores, the sample may be transferred directly to the distillation flask by means of concentrated, arsenic-free hydrochloric acid. If a preliminary separation of other metals has been made and arsenic is present (along with antimony and tin) as a sulphide, it is oxidized by addition of concentrated HCl and sufficient potassium chlorate to cause solution and oxidation of free sulphur, and the chlorate decomposed by evaporation to dryness; or if preferred, by evaporation of the alkaline solution to dryness, oxidation with fuming nitric and re-evaporation to dryness to expel the nitric acid. The residue is taken up with hydrochloric acid and washed into the flask with strong hydrochloric acid as directed above.

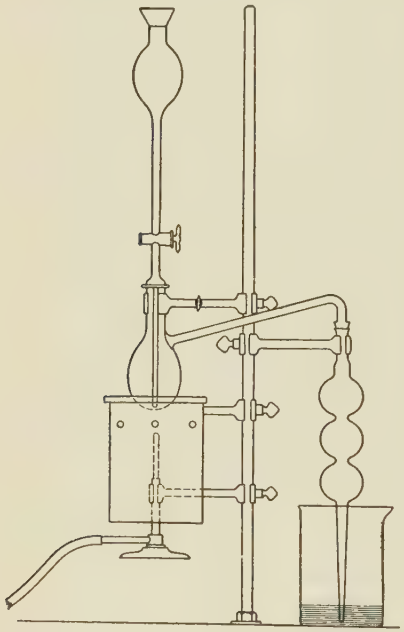


Fig. 44. Knorr Arsenic Distillation Apparatus.

**Distillation.** — The sample, in a half-liter distilling flask (Fig. 44) is made up to about 150 cc. with concentrated hydrochloric acid and about 5 grams of cuprous chloride, $Cu_2Cl_2$, are added. The apparatus is connected up as shown in the illustration, and arsenious chloride distilled from the solution according to the method outlined under the illustration.

Arsenic may be determined in the distillates either gravimetrically or volumetrically. The volumetric procedures for arsenic, in this isolated form, are generally to be preferred, since they are both rapid and accurate. For amounts over 0.5% arsenic, the iodine method is recommended, for smaller amounts (arsenic in crude copper), precipitation with silver nitrate and titration of the silver salt is best. Exceedingly small amounts are best determined by the Gutzeit method.

The inlet funnel is filled about half full with hydrochloric acid (sp. gr. 1.2). The outlet of the condenser tube is caused to dip just beneath the surface of 100 cc. of distilled water, containing a lump of ice. The solution in the distillation flask is heated to boiling; concentrated hydrochloric acid is introduced through the funnel drop by drop at the rate sufficient to replace the evaporation. All the arsenic usually distils over in half an hour. At this time the beaker holding the condensate is replaced by another with 100 cc. of water. And the distillation continued about 15 minutes. Test this distillate to ascertain whether any arsenic is present.

### Separation of Arsenic from Antimony and Tin by Precipitation as Sulphide in a Strong Hydrochloric Acid Solution

This procedure for isolation of arsenic depends upon the insolubility of the sulphide of arsenic in strong hydrochloric acid, whereas that of antimony dissolves. The sulphide of tin is also soluble.

**Procedure.** — The metals present in their lower conditions of oxidation are precipitated as sulphides in presence of dilute hydrochloric acid (5% solution) to free them from subsequent groups (Fe, Al, Ca, etc.). The soluble members of the hydrogen sulphide group are now dissolved and separated from copper, lead, etc., by caustic as follows: The greater part of the washed precipitate is transferred to a small casserole, that remaining on the filter paper is dissolved off by adding to it a little hot dilute potash solution, catching the filtrate in the casserole. About 5 grams weight of solid potassium hydroxide or sodium hydroxide is added to the precipitate. Arsenic, antimony, and tin sulphides dissolve. The solution is filtered if a residue remains, and the filter washed. This preliminary treatment is omitted if alkaline earths and alkalies are the only contaminating elements present, or in case a separate solution is used for determining the other elements of the $H_2S$ group. Acidification of the alkali extract will precipitate tin, antimony and arsenic, if the acidity does not exceed 2.5% free HCl. The sulphides are filtered off and treated with hydrochloric acid (sp. gr. 1.135) made by diluting 2 volumes of strong HCl with one of water. Upon digesting on a hot water bath for a few minutes antimony and tin go into solution, while arsenic remains insoluble. The solution is saturated with $H_2S$ gas to insure the complete precipitation of arsenic and the sulphide filtered off, and washed with HCl (2:1 containing $H_2S$).

**Optional Method.** — Hydrogen sulphide gas is passed into a solution of arsenic containing two parts of strong HCl to one of water. Arsenic alone will precipitate; antimony and tin, if present, will remain in solution.

The sulphide may be dissolved in concentrated sulphuric acid by heating to sulphuric acid fumes and until the solution becomes clear. No arsenic is lost, provided the heating is not unduly prolonged. Fifteen to twenty-five minutes is generally sufficient to dissolve the sulphide and expel $SO_2$, etc. The acid may be neutralized with ammonia or caustic, made again barely acid and then alkaline with bicarbonate of soda, and arsenous acid titrated with iodine.

## GRAVIMETRIC METHOD FOR ARSENIC

### DETERMINATION OF ARSENIC AS MAGNESIUM PYROARSENATE

The method worked out by Levol depends upon the precipitation of arsenic as $MgNH_4AsO_4 \cdot 6H_2O$, when magnesia mixture is added to an ammoniacal solution of the arsenate. Although 600 parts of water dissolve 1 part of the salt, it is practically insoluble in a $2\frac{1}{2}$ per cent ammonia solution, 1 part of the anhydrous salt requiring 24,558 parts of the ammonia water according to Virgili. The compound loses $5\frac{1}{2}$ molecules of water at 102° C. and all of the water when strongly ignited, forming in presence of oxygen the stable magnesium pyroarsenate, $Mg_2As_2O_7$, in which form arsenic is determined.

**Procedure.** — The solution containing the arsenic, in the form of arsenate, and having a volume not exceeding 100 cc. per 0.1 gram arsenic present, is treated with 5 cc. of concentrated hydrochloric acid, added, with constant stirring, drop by drop. Ten cc. of magnesia mixture are added (Reagent = 55 grams $MgCl_2 + 70$ grams $NH_4Cl + 650$ cc. $H_2O$ and made up to 1000 cc. with $NH_4OH$, sp.gr. 0.96), for each 0.1 gram of arsenic present. Ammonia solution (sp.gr. 0.96) is added from a burette, with stirring, until the mixture is neutralized (a red color imparted to the solution in presence of phenolphthalein indicator), and then ammonia added in excess equal to one-third the volume of the neutralized solution. The precipitate is allowed to settle at least twelve hours and is then filtered into a weighed Gooch crucible and washed with 2.5% ammonia until free from chloride. After draining as completely as possible by suction the precipitate is dried at 100° and then heated to a dull red heat (400 to 500° C.), preferably in an electric oven, until free of ammonia. The temperature is then raised to a bright red heat (800 to 900° C.) for about ten minutes, the crucible then cooled in a desiccator and the residue weighed as $Mg_2As_2O_7$.

Factors, $Mg_2As_2O_7 \times 0.4827 = As$, or $\times 0.6373 = As_2O_3$, or $\times 0.7403 = As_2O_5$ or $\times 0.7925 = As_2S_3$.

Notes. In place of an electric furnace the Gooch crucible may be placed in a larger non-perforated crucible, the bottom of the Gooch being 2–3 mm. above the bottom of the outer crucible. The product may now be heated in presence of a current of oxygen passed through a perforation in the covering lid of the Gooch, or Rose crucible.

## VOLUMETRIC METHODS FOR THE DETERMINATION OF ARSENIC

### OXIDATION OF THE ARSENOUS ACID WITH STANDARD IODINE

This procedure is applicable for the determination of arsenic in acids, after reduction of arsenic to its arsenous form, for valuation of arsenic in the trioxide, for determination of arsenic isolated by distillation as arsenous chloride, for arsenic in arsenites and reduced arsenates in insecticides, etc. The method depends upon the reaction $As_2O_3 + 2H_2O + 2I_2 = As_2O_5 + 4HI$. The liberated hydriodic acid is neutralized by sodium bicarbonate. The trace of excess iodine is detected by means of starch, a blue color being produced.

Consult " Preparation and Solution of the Sample " for the special material tested and directions for isolation of arsenic by distillation (page 101) or by precipitation in a strong HCl solution as $As_2S_3$. Prepare the solution as directed and complete the determination as follows:

**Procedure.** — If the solution is acid, it is neutralized by sodium or potassium hydroxide or carbonate (phenolphthalein indicator) then made slightly acid. If the solution is alkaline, it is made slightly acid. Two to 3 grams of sodium bicarbonate are added together with starch indicator and the solution titrated with tenth normal iodine solution, the iodine being added cautiously from a burette until a permanent blue color develops.

One cc. N/10 iodine = 0.00375 gram As, or 0.004948 gram $As_2O_3$.

$As_2O_3 \times 1.1616 = As_2O_5$. $As \times 1.3201 = As_2O_3$ or $\times 1.5336 = As_2O_5$

$As_2O_3 \times 0.7575 = As$.

## POTASSIUM IODATE METHOD FOR DETERMINING ARSENIC[1]

The method is specially applicable to determining arsenic in insecticides. The reaction is represented as follows:

$$As_2O_3 + KIO_3 + 2HCl = As_2O_5 + ICl + KCl + H_2O.$$

**Procedure.** — In determining total arsenic the sample is placed in a distilling bulb, connected to a condenser, strong hydrochloric acid added together with cuprous chloride, and arsenious chloride distilled over into an Erlenmeyer flask according to the standard procedure. If arsenic is high, an aliquot portion of the distillate is taken and the titration made with standard iodate solution.

For determining arsenious oxide in Paris Green or other arsenite 0.15 to 0.4 grams of the sample may be weighed directly into a glass-stoppered bottle (500 cc.) and the titration made.

**Iodate Titration.** — 30 cc. of hydrochloric acid sp.gr. 1.19, 20 cc. of water and 6 cc. of chloroform are added to the solid arsenite. If the arsenic is in solution, sufficient HCl should be present to have the acidity between 11 and 20 per cent HCl. (If this falls below 11% HCl hydrolysis of the iodine monochloride will take place. If over 20% HCl the reaction proceeds very slowly.) Potassium iodate solution is now added, rapidly at first, shaking the contents of the bottle. When the iodine that has been liberated during the first part of the titration has largely disappeared from the solution, the stopper of the bottle is inserted and the contents thoroughly shaken. The titration is now conducted cautiously, shaking thoroughly with each addition of the reagent. The titration is complete when after shaking and allowing to stand 5 minutes no color is observed in the chloroform.

**Reagent.** — Contains 3.244 g. of $KIO_3$ (dried at 140° C.) per 1000 cc. — 1 cc. = 0.003 g. $As_2O_3$.

[1] Geo. S. Jamison, J. I. E. C. **10**, 290–292, 1918.

## DETERMINATION OF ARSENIC IN ORES

### PRECIPITATION OF ARSENIC AS SULPHIDE IN A STRONG HYDROCHLORIC ACID SOLUTION

Details for isolation of arsenic as $As_2S_3$ thus separating it from other elements, including antimony and tin, are given in the chapter on Antimony. The ore (0.5 to 1.0 gram) is decomposed by fusion with acid sodium sulphate and sulphuric acid, the arsenic being reduced by adding a small piece of filter paper. The cooled melt is dissolved in about 25 cc. of water and 50 cc. of strong HCl and the arsenic precipitated as sulphide, $As_2S_3$, by saturating the solution with $H_2S$. Antimony and the other elements remain in solution. The sulphide is filtered off and washed with a 2:1 solution of HCl seven or eight times and then with $H_2S$ wa er to remove the chlorides.

The sulphide is now dissolved with a 5% solution of sodium hydroxide catching the solution in the flask in which the fusion was made. Then the procedure is as follows:

To the solution in the flask is added about 3 grams of sodium sulphate and 10 cc. of strong $H_2SO_4$ and it is boiled to small bulk, then heated over free flame, precisely as in the original decomposition, until all free acid and free sulphur are expelled and a clear melt is obtained, which is allowed to cool. When cold, the melt is dissolved in 50 cc. of hot water and boiled a minute or two, to expel any possible $SO_2$, then again cooled under the tap to room temperature.

A few drops of phenolphthalein solution are added, the solution made slightly alkaline with sodium hydroxide, then re-acidified slightly with HCl. Finally, 3–4 grams, of sodium acid carbonate, are added cooling again if the solution is warm. The arsenic is now titrated with standard iodine solution to a permanent blue tinge, in presence of starch indicator.

One cc. N/10 iodine = 0.00375 gram arsenic.

## DETERMINATION OF SMALL AMOUNTS OF ARSENIC

### MODIFIED GUTZEIT METHOD[1]

The following procedure furnishes a rapid and accurate method for determination of exceedingly small amounts of arsenic ranging from 0.001 milligram to 0.5 milligram $As_2O_5$. It is more sensitive and less tedious than the Marsh test. The details, given below with slight modifications, have been carefully worked out in the laboratories of the General Chemical Company and have proved exceedingly valuable in estimating small amounts of arsenic in acids, bases, salts, soluble arsenic in lead arsenate and zinc arsenite and other insecticides, traces of arsenic in food products, baking powders, canned goods, etc.

The method depends upon the evolution of arsine by the action of hydrogen on arsenic compounds under the catalytic action of zinc, the reaction taking place either in alkaline or acid solutions. The evolved arsine reacts with mercuric chloride, forming a colored compound. From the length and intensity of the color stain the amount of arsenic is estimated by comparison with standard stains.

Although the acidity of the sample and the amount of zinc shot should be kept within certain limits, the results are not affected by slight variation as was formerly thought. The physical characteristics of the zinc used rather than the surface exposed to acid action appears to have an effect on the evolution of arsine. The best results are obtained with zinc having a finely crystalline structure.

Iron present in the solution tends to prevent evolution of stibine, but has no apparent effect on arsine generation.

Stannous chloride is essential to the complete evolution of arsine, hence this reagent is added to the solution in which arsenic is determined.

Antimony present in the solution in amounts less than 0.0001 gram, does not interfere with the determination of arsenic. If a greater amount of antimony is present a separation of arsenic should be made by distillation. The following modification of the method given on page 101 is recommended. Air saturated with HCl, by pass-

[1] The accuracy of the Gutzeit method is within 10 % of the truth.

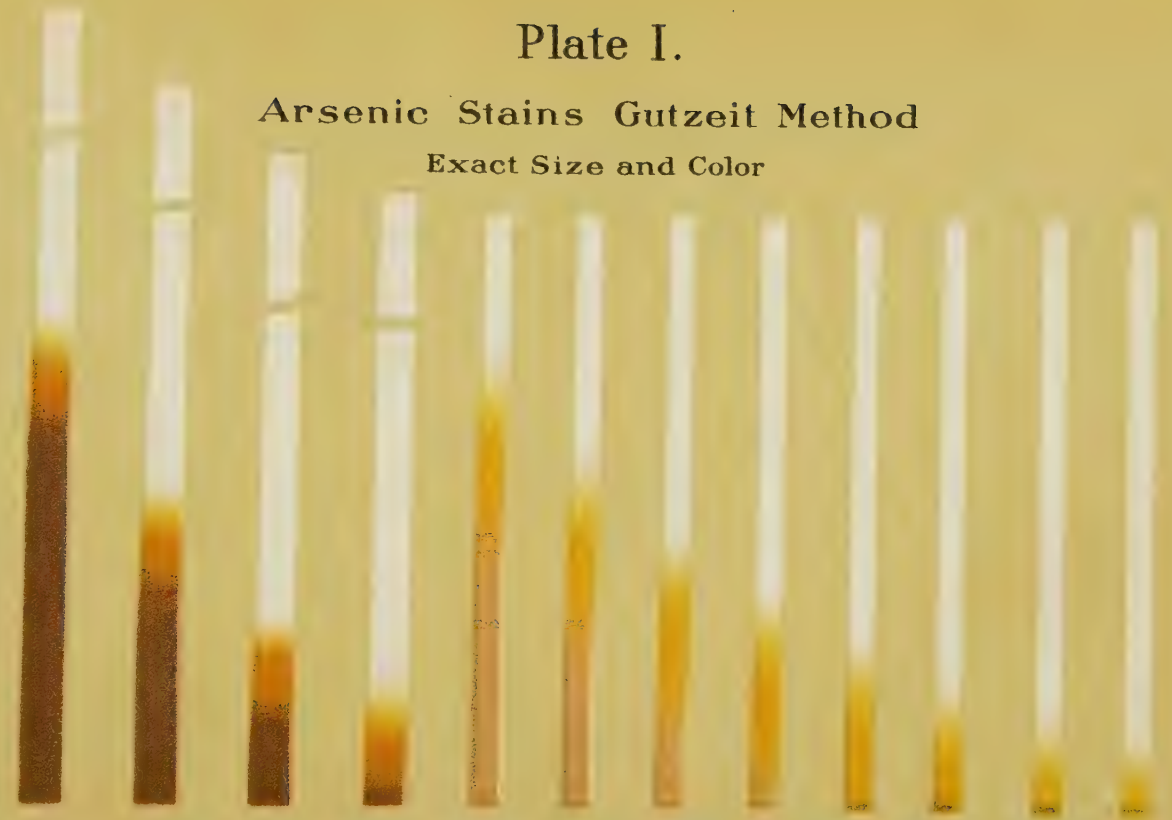
Evolution of arsine by the electrolytic method, in place of the method outlined, proved to be unreliable. The evolution of arsine is effected by the slightest variation in conditions so it is extremely difficult to obtain concordant results.

**Marsh Method.** — In the *Marsh* test arsine is passed through a glass tube constricted to capillarity. By application of heat the arsine is decomposed and metallic arsenic deposited. The tube is heated just before the capillary constriction so that arsenic deposits in the drawn out tube. Comparison is made with standards, the length of the stain being governed by the amount of arsenic in the evolved gas. Slight variations in the size of the capillary tube and rate of evolution make a notable variation in length of stain.

# Plate I.

## Arsenic Stains Gutzeit Method

Exact Size and Color




The numerals represent milligrams $As_2O_3$ causing the stain

ing it through a gas wash bottle containing concentrated hydrochloric acid, is drawn through the boiling solution containing the sample in a saturated HCl solution, reduction of arsenic to arsenious chloride having been effected with cuprous chloride as prescribed. The air sweeps the arsine into the water in the receiving flasks. It is advisable to have two flasks connected in series. Gentle suction is applied at the receiving end of the train. The apparatus may be made in fairly compact form.

**Special Reagents. Standard Arsenic Solution.** — One gram of resublimed arsenous acid, $As_2O_3$, is dissolved in 25 cc. of 20% sodium hydroxide solution (arsenic-free) and neutralized with dilute sulphuric acid. This is diluted with fresh distilled water, to which 10 cc. of 95% $H_2SO_4$ has been added, to a volume of 1000 cc. Ten cc. of this solution is again diluted to a liter with distilled water containing acid. Finally 100 cc. of the latter solution is diluted to a liter with distilled water containing acid. One cc. of the final solution contains 0.001 milligram $As_2O_3$.

**Standard Stains.** — Two sets of stains are made, one for the small apparatus for determining amounts of $As_2O_3$ ranging from 0.001 to 0.02 milligram, and a second set for the larger-sized apparatus for determining 0.02 to 0.5 milligram $As_2O_3$. Stains made by $As_2O_3$ in the following amounts are convenient for the standard sets; e.g., small apparatus, 0.001, 0.002, 0.004, 0.006, 0.01, 0.015, 0.02 milligram $As_2O_3$. Large apparatus, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 milligram $As_2O_3$.

In making the stain the requisite amount of standard reagent, $As_2O_3$ solution, is placed in the Gutzeit bottle with the amounts of reagents prescribed for the regular tests and the run made exactly as prescribed in the regular procedure.

**Preservation of the Stains.** — The strips of sensitized paper with the arsenic stain are dipped in molten paraffine (free from water), and mounted on a sheet of white paper, folded back to form a cylinder. The tube is placed in a glass test-tube containing phosphorus pentoxide, which is then closed by a stopper. It is important to keep the stained strip dry, otherwise the stain soon fades, hence the paper on which the strips are mounted and the glass test-tube, etc., must be perfectly dry. It is advisable to keep the standard in a hydrometer case, while not in use, as light will gradually fade the color.

**Sensitized Mercuric Chloride (or Bromide) Paper.** — $20 \times 20$ in. Swedish Filter Paper No. 0 is cut into four equal squares. For use in the large Gutzeit apparatus the paper is dipped into a 3.25% solution of mercuric chloride (mercuric bromide may be used in place of the chloride) or if it is to be used in the small Gutzeit apparatus it is dipped into a 0.35% mercuric chloride solution. (The weaker the solution, the longer and less intense will be the stain.) The paper should be of uniform thickness, otherwise there will be an irregularity in length of stain for the same amounts of arsenic. (The thicker the paper the shorter the stain. The paper is hung up and dried in the

air, free from gas fumes, $H_2S$ being particularly undesirable.) When dry, half an inch of the outer edge is trimmed off (since this is apt to contain more of the reagent), and the paper cut into strips. The paper with more concentrated reagent is cut into strips 13 cm. by 5 mm. and that with 0.5% mercuric chloride into strips 7 cm. by 4 mm. The paper is preserved in bottles with tight-fitting stoppers.

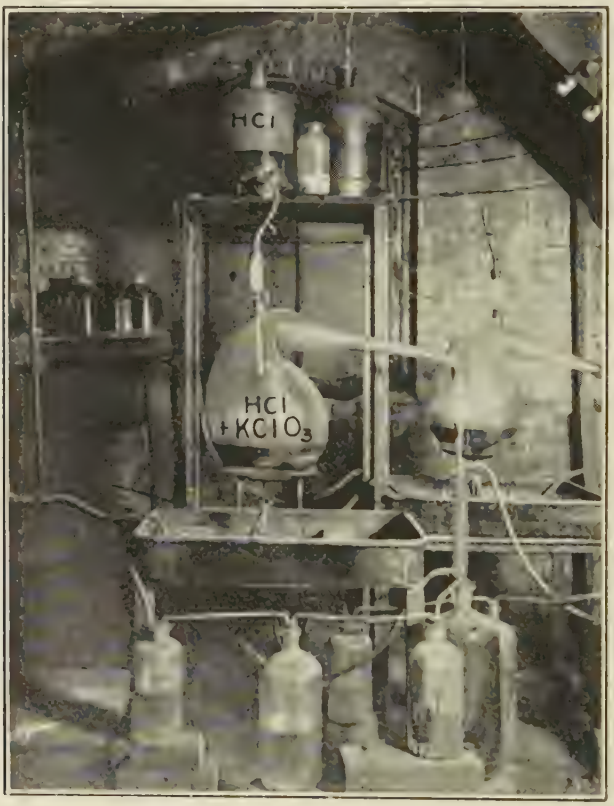



FIG. 45. Purification of Hydrochloric Acid.

Standards should be made with each batch of paper. Paper with a white deposit of $HgCl_2$ should not be used.

**Ferric Ammonium Alum.** — Eighty-four grams of the alum with 10 cc. of mixed acid is dissolved and made up to a liter. Ten cc. of this solution contains approximately 0.5 gram $Fe_2O_3$.

**Lead Acetate.** — One per cent solution with sufficient acetic acid to clear the solution.

**Zinc.** — Arsenic free zinc shot, size 0.13 to 0.3 inch. The zinc is treated with C. P. hydrochloric acid, until the surface of the zinc becomes clean and dull. It is then washed, and kept, in a casserole, covered with distilled water, a clock-glass keeping out the dust.

**Mixed Acid.** — One volume of arsenic-free $H_2SO_4$ is diluted with four volumes of pure water and to this are added 10 grams of NaCl per each 100 cc. of solution.

**Stannous Chloride.** — Eighty grams of stannous chloride dissolved in 100 cc. of water containing 5 cc. of arsenic-free hydrochloric acid (1.2 sp.gr.).

**Arsenic-free Hydrochloric Acid.** — The commercial acid is treated with potassium chlorate to oxidize the arsenic to its higher form and the acid distilled. The distilling apparatus may be arranged so that a constant distillation takes place, acid from a large container dropping slowly into a retort containing potassium chlorate, fresh hydrochloric acid being supplied as rapidly as the acid distills. See Fig. 45.

**Lead Acetate Test Paper for Removal of $H_2S$.** — Large sheets of qualitative filter paper are soaked in a dilute solution of lead acetate and dried. The paper is cut into strips $5 \times 7$ cm.

Blanks should be run on all reagents used for this work. The reagents are arsenic-free if no stain is produced on mercuric chloride paper after forty-five minutes' test.

**Special Apparatus.** — The illustration, Fig. 46, shows the Gutzeit apparatus connected up, ready for the test. The dimensions on the left-hand side are for the small apparatus and those on the right for the large form. Rubber stoppers connect the tubes to the bottle. The apparatus consists of a wide-mouth 2-oz. or 8-oz. bottle according to whether the small or large apparatus is desired, a glass tube (see Fig. 46) containing dry lead acetate paper and moist glass wool for removal of traces of hydrogen sulphide and a small-bore tube containing the strip of mercuric chloride paper.

### Preparation of the Sample for Determining Traces of Arsenic

The initial treatment of the sample is of vital importance to the Gutzeit Method for determining traces of arsenic. The following procedures cover the more important materials or substances in which the chemist will be called upon to determine minute amounts of arsenic.

**Traces of Arsenic in Acids.** — The acid placed in the Gutzeit apparatus should be equivalent to 4 2 grams of sulphuric acid or 3.1 grams of hydrochloric acid and should contain 0.05 to 0.1 gram $Fe_2O_3$ equivalent. If large samples are required for obtaining the test it is necessary either to expel a portion of the acid in order to obtain the above acidity or to make standard stains under similar conditions of acidity. It must be remembered that arsenous chloride is readily volatile,

whereas the arsenic chloride is not, hence it is necessary to oxidize arsenic before attempting to expel acids. If nitric acid or bromine or chlorine (chlorate) be added for this purpose, it must be expelled before attempting the Gutzeit test. Nitric acid may be expelled by adding sulphuric acid and taking to $SO_3$ fumes. Free chlorine, bromine, or iodine will volatilize on warming the solution. Chlorine in a chlorate is expelled by taking the sample to near dryness in presence of free acid. Sulphurous acid or hydrogen sulphide, if present, should be expelled by boiling the solution, then making faintly pink with $KMnO_4$ and destroying the excess with a drop or so of oxalic acid. $SO_2$ is reduced by zinc and hydrogen to $H_2S$, which forms black HgS with mercuric chloride, hence removal of $SO_2$ and $H_2S$ are necessary before running the test.

**Sulphuric Acid.** — With amounts of arsenic exceeding 0.00005% $As_2O_3$, 5 to 10 grams of acid, according to its strength, are taken for analysis and diluted to 15 or 20 cc. If $H_2S$ or $SO_2$ are present, expel by boiling for fifteen or twenty minutes. Prolonged fuming of strong acid should be avoided by previously diluting the acid with sufficient water. In mixed acid containing nitric acid the sample is taken to $SO_3$ fumes to expel nitric acid. The procedure given later for the regular determination is now followed.

For estimating very minute amounts of arsenic, 0.000005 to 0.00005% $As_2O_3$, it is necessary to take a 25- to 50-gram sample for analysis. The acid is treated as directed above for removal of $H_2S$ or $SO_2$ or nitric acid and diluted in the Gutzeit apparatus to at least 130 cc., using the large apparatus. Upon the addition of iron and stannous chloride follow directions in the procedure described on page 113 for large Gutzeit test. The stains are compared with standard stains produced by known amounts of arsenic added to 50-gram portions of arsenic-free sulphuric acid of strength equal to that of the sample. The stains are longer and less intense than those produced by less acid.

**Hydrochloric Acid.** — Twenty cc. is taken for analysis (sp.gr. being known); the sample should contain an acid equivalent of about 3.1 grams of hydrochloric acid. Chlorine is expelled by bubbling air through the acid before taking a sample. The procedure is given for further treatment of the sample following the section on preparation of the sample.

**Nitric Acid.** — One hundred cc. of the acid (sp.gr. being known) is evaporated with 5 cc. of concentrated sulphuric acid to $SO_3$ fumes, to expel nitric acid. Arsenic is determined in the residue by the standard procedure.

**Phosphates, Phosphoric Acid.** — Arsenic, in phosphoric acid, combined or free, cannot be determined in the usual way, as $P_2O_5$ has a retarding effect upon the evolution of arsine, so that the results are invariably low, small amounts of arsenic escaping detection. Arsenic, however, may be volatilized from phosphates and phosphoric acid, as arsenous chloride, $AsCl_3$, in a current of hydrogen chloride

by heating to boiling. One gram or more of the phosphate is placed in a small distilling flask, connected directly to a 6-in. coil condenser dipping into the Gutzeit bottle, containing 20 to 30 cc. of cold distilled water. A second bottle connected in series may be attached for safeguarding loss (this seldom occurs). Fifty cc. of concentrated hydrochloric acid are added to the sample and 5 grams of cuprous chloride. Arsenic is distilled into the Gutzeit bottle by heating the solution to boiling and passing a current of air through strong hydrochloric acid into the distilling flask by applying suction at the receiving end of the system. All of the arsenic will be found in the first 10 or 15 cc. of the distillate. Arsenic may now be evolved after addition of iron, stannous chloride and zinc, as directed in the procedure.

**Salts, Sodium Chloride, Magnesium Sulphate, etc.** — One-gram samples are taken and dissolved in a little water and an equivalent of 4.2 grams of sulphuric acid added. The solution of iron and stannous chloride having been added, the run is made with 5 cc. of zinc shot, placed in the Gutzeit bottle.

### PROCEDURE FOR MAKING THE TEST

For amounts of arsenic varying from 0.001 milligram to 0.02 milligram $As_2O_3$, the small apparatus is used. The volume of the solution should be 50 cc. It should contain an equivalent of 4.2 grams sulphuric acid and should have about 0.1 gram equivalent of $Fe_2O_3$ reduced by 0.5 cc. of stannous chloride solution. Arsine is generated by adding one 5-cc. crucible of arsenic-free zinc shot, $\frac{1}{3}$ to $\frac{1}{6}$-inch mesh. Temperature 75 to 80° F.

For amounts ranging from 0.02 to 0.5 milligram $As_2O_3$,[1] the large apparatus is used. The volume of the solution should be about 200 cc. and should contain an equivalent of 18.5 grams of sulphuric acid and should have 0.1 gram equivalent of $Fe_2O_3$, reduced by 0.5 cc. stannous chloride solution. Arsine is generated by adding one 12-cc. crucible of zinc shot ($\frac{1}{3}$ to $\frac{1}{6}$-inch mesh.) The temperature should be 105° F. The sample taken should be of such size that a stain is obtained equivalent to that given by 0.1 to 0.5 milligram $As_2O_3$.

[1] It is advisable to use smaller samples when the arsenic content is over 0.3 milligram $As_2O_3$, as the longer stains are unreliable.

Ferrous iron prevents polarization between zinc and the acid and hence aids in the evolution of arsine.

In the analysis of baking powders, bauxite, sodium or similar salts, the distillation method is recommended.

Hydrochloric acid is used in place of sulphuric acid in cases where complete solution by the latter acid cannot be effected.

Standards and samples should be run under similar conditions, temperature, acidity, amount of zinc, volume of solution, etc. In place of zinc shot, zinc rods, cubes or discs may be used for generating arsine and hydrogen.

Lead acetate paper is placed in the lower portion of tube *B;* the upper portion of *B* contains glass wool moistened with lead acetate solution; the tube *A* contains the test strip of mercuric chloride paper. See Fig. 46. Immediately upon adding the required amount

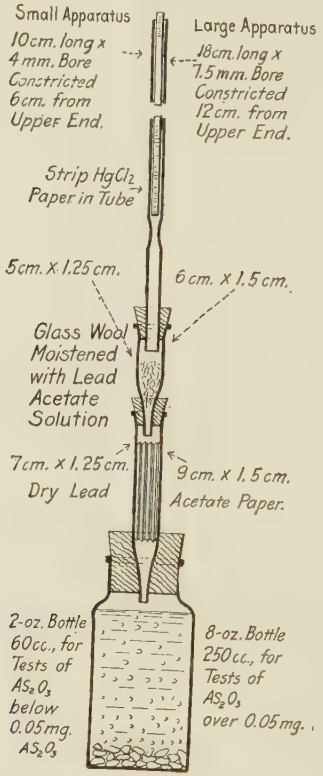



Fig. 46. Gutzeit Apparatus for Arsenic Determination.

of zinc to the solution in the bottles, the connected tubes are put in position, as shown in the illustration, and the bottle gently shaken and allowed to stand for one hour for the small apparatus, forty minutes for the large. The test paper is removed, dipped in molten paraffin and compared with the standard stains. See Plate I.

*Estimation of Per cent.* $\dfrac{\text{The milligram } As_2O_3 \text{ stain} \times 100}{\text{Weight of sample taken}} = \%\ As_2O_3.$

## BARIUM

**Ba, at.wt. 137.37; sp.gr. 3.78; m.p. 850° C.; volatile at 950° C.; oxides, BaO, $BaO_2$**

The determination of barium is required in the valuation of its ores, barite, heavy spar, $BaSO_4$; witherite, $BaCO_3$; baryto calcite, $BaCO_3.CaCO_3$. It is determined in certain white mixed paints and colored pigments, Venetian, Hamburg or Dutch whites, chrome paints, etc. In analysis of Paris green, baryta insecticides, putty, asphalt, dressings and pavement surfacings. It may be found as an adulterant in foods, wood preservatives, filler in rubber, rope, fabrics. It is determined in salts of barium. The nitrate is used in pyrotechny, in mixtures for green fire.

### OCCURRENCE

Barium is found only combined in nature.

**Minerals.** — Those of commercial importance are:

**Witherite,** $BaCO_3$, white or gray, translucent mineral with vitreous lustre; granular or columnar crystals resembling quartz; white streak; hardness 3–4.

**Barite,** $BaSO_4$, a heavy, white or light colored mineral of vitreous or pearly lustre; transparent to opaque; brittle; white streak; hardness 2.5–3.5.

### DETECTION

Prepare a solution for the qualitative tests by dissolving the sample in hydrochloric acid. If this does not effect solution fuse the material with sodium-potassium carbonate mixture 1:1, extract the cooled fusion with hot water and wash the residue on a filter thoroughly with water. (Reject the filtrate.) Dissolve the carbonate residue in dilute hydrochloric acid and test this solution for barium, using separate portions of the solution.

**Precipitation as Sulphate, Sulphuric Acid Test.** — Barium sulphate is precipitated by addition of a soluble sulphate to a solution of a barium salt. The compound is extremely insoluble in water and in dilute acids (soluble in hot concentrated sulphuric acid). The sulphate is readily distinguished from lead sulphate by the fact that the latter is soluble in ammonium salts, whereas barium sulphate is practically insoluble.

**Precipitation as Carbonate.** — Remove previous groups by saturating the solution with hydrogen sulphide, filtering off the sulphides of the second group (Hg, Pb, Cu, Bi, As, Sb, Sn etc.). Make the filtrate

alkaline with ammonia and again filter off the members of the third group (Fe, Mn, Al, Co, Ni, Cr, Zn etc.). Acidify the filtrate with hydrochloric acid, boil out $H_2S$ gas.

Barium is precipitated as the carbonate together with strontium and calcium by addition of ammonium hydroxide and ammonium carbonate to the filtrate of the ammonium sulphide group. It is separated from strontium and calcium by precipitation as yellow barium chromate, $BaCrO_4$, from a slightly acetic acid solution.

**Saturated solutions of calcium or strontium sulphates** precipitate white barium sulphate, $BaSO_4$, from its chloride or nitrate or acetate solution, barium sulphate being the least soluble of the alkaline earth sulphates.

**Soluble chromates** precipitate yellow barium chromate from its neutral or slightly acetic acid solution, insoluble in water, moderately soluble in chromic acid, soluble in hydrochloric or nitric acid.

**Fluosilicic acid, $H_2SiF_6$,** precipitates white, crystalline barium fluosilicate, $BaSiF_6$, sparingly soluble in acetic acid, insoluble in alcohol. (The fluosilicates of calcium and strontium are soluble.)

**Flame.** — Barium compounds color the flame yellowish green, which appears blue through green glass.

**Spectrum.** — Three characteristic green bands ($\alpha$, $\beta$, $\gamma$).

See chapter on Calcium for Rapid Preliminary Test showing Barium, Strontium and Calcium.

### Suggestions for Students

Read carefully the sections on "Detection" of barium, "Preparation of the Sample" and "Separations." For laboratory work determine barium in a soluble barium salt such as barium chloride or nitrate following the directions given on page 123.

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

Compounds of barium, with the exception of the sulphate, $BaSO_4$, are soluble in hydrochloric and nitric acids. The sulphate is soluble in hot concentrated sulphuric acid, but is reprecipitated upon dilution of the solution. The sulphate is best fused with sodium carbonate, which transposes the compound to barium carbonate; sodium sulphate may now be leached out with water and the residue, $BaCO_3$, then dissolved in hydrochloric acid.

**Solution of Ores. Sulphates.** — 0.5 to 1 gram of the finely divided ore is fused with 3 to 5 grams of sodium and potassium carbonate mix, 2 : 1, or sodium carbonate alone, in a platinum dish. (Prolonged fusion is not necessary.) The melt is cooled and then extracted with hot water. See following method.

# Emmissions-Spectra

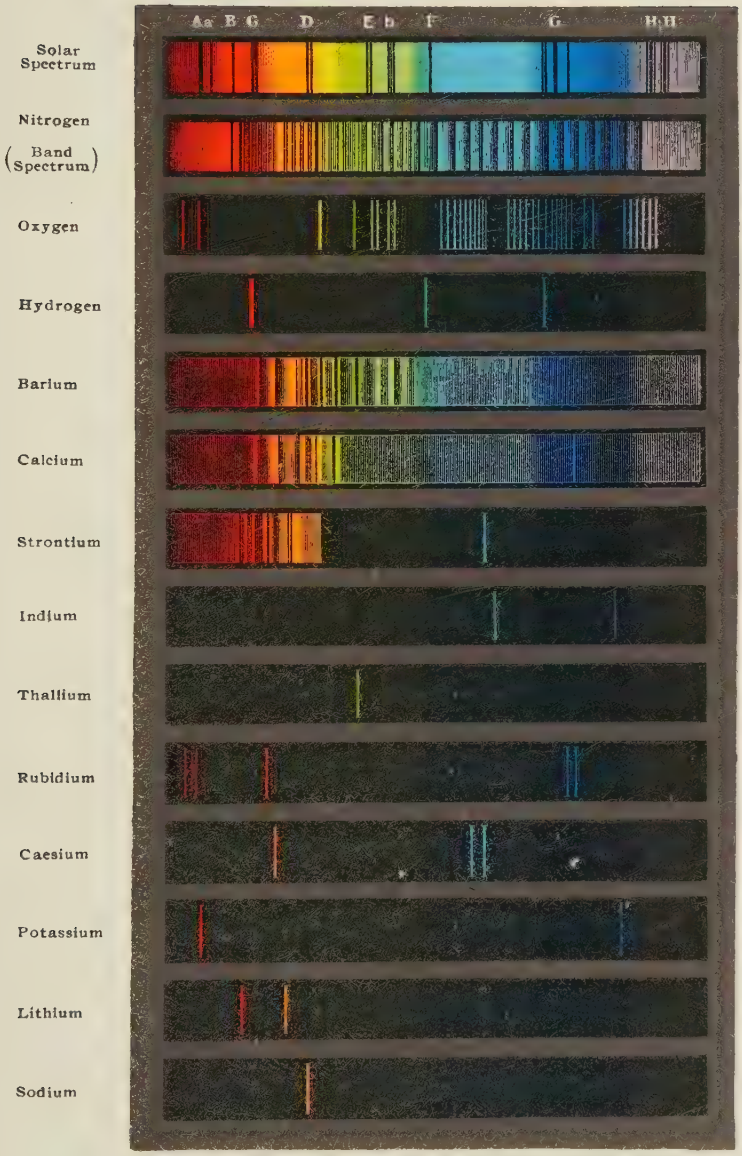



Plate II.

**Barium in Insoluble Residue.** — In the complete analysis of ores the residue remaining insoluble in acids is composed largely of silica, together with difficultly soluble substances, among which is barium sulphate. This residue is best fused in a platinum dish with sodium carbonate or a mixture of sodium and potassium carbonates (long fusion is not necessary). The cooled mass is digested with hot water to remove the soluble sodium compounds, silicate being included. Barium, together with the heavy metals, remains insoluble as carbonate and may be filtered off. The residue is now treated with dilute ammonia water to remove the adhering sulphates (testing the filtrate with hydrochloric acid and barium chloride solution, the washing being complete when no white precipitate of barium sulphate forms). The carbonates are washed off the filter into a 500-cc. beaker, the clinging carbonate being dissolved by pouring a few cc. of dilute, 1 : 1, hydrochloric acid on the paper placed in the funnel. This extract is added to the precipitate in the beaker and the latter covered to prevent loss by spattering. Additional hydrochloric acid is cautiously added so that the precipitate completely dissolves and the solution contains about 10 cc. of free hydrochloric acid (sp.gr. 1.2). Barium is precipitated from this solution best as a sulphate according to directions given later.

**Silicates.** — One gram of the finely pulverized sample is treated with 10 cc. of dilute sulphuric acid, 1 : 4, and 5 cc. of strong hydrofluoric acid. The mixture, evaporated to small bulk on the steam bath, is taken to $SO_3$ fumes on the hot plate. Additional sulphuric acid and hydrofluoric acid are used if required. By this treatment the silica is expelled and barium, together with other insoluble sulphates, will remain upon the filter when the residue is treated with water and filtered. Lead sulphate, if present, may be removed by washing the residue with a solution of ammonium acetate. Barium sulphate may be purified by fusion with potassium carbonate as above directed or by dissolving in hot concentrated sulphuric acid, and precipitating again as $BaSO_4$ by dilution.

**Sulphides.** — The ore is oxidized, as directed for pyrites under the subject of sulphur. After the removal of the soluble sulphates, the residue, containing silica, barium, and small amounts of insoluble oxides, is fused and dissolved according to the procedure for sulphates.

**Carbonates.** — In absence of sulphates the material may be dissolved with hydrochloric acid, taken to dryness to dehydrate silica and after heating for an hour in the steam oven (110° ±) the residue is extracted with dilute hydrochloric acid and filtered. The filtrate is examined for barium according to one of the procedures given later.

**Salts Soluble in Water.** — Nitrates, chlorides, acetates, etc., are dissolved with water slightly acidulated with hydrochloric acid.

**Material Containing Organic Matter.** — The substance is roasted to destroy organic matter before treatment with acids or by fusion with the alkali carbonates.

## The Alkaline Earths

**Preliminary Considerations.** — In the determination of barium, calcium, and strontium, the following causes may lead to loss of the elements sought:

*a. Presence of Phosphates.* Phosphoric acid, free or combined, has a decided influence upon the determination of the members of this group. Combined as phosphate it will cause the complete precipitation of barium, calcium, and strontium, along with iron, alumina, etc., upon making the solution alkaline for removal of the ammonium sulphide group. It is a common practice to hold up the iron + alumina by means of tartaric, citric, or other organic acids before making ammoniacal for precipitation of this group as oxalates, or again the basic acetate method is used for precipitation of iron and alumina; calcium, barium, and strontium going into solution. These procedures may be satisfactory for the analysis of phosphate rock and similar products, but do not cope with the difficulty when large amounts of phosphates are present. In samples containing free phosphoric acid, barium, calcium, and strontium, present in small amounts, may remain in solution in presence of sulphates or oxalates. Appreciable amounts of calcium, 1% or more, may escape detection by the usual method of precipitation by ammonium oxalate added to the alkaline solution, on account of this interference, so that the removal of phosphoric acid before precipitation of this group is frequently necessary. This may be accomplished by addition of potassium carbonate in sufficient excess to combine completely with the phosphoric acid and form carbonates with the bases. The material taken to dryness is fused with additional potassium carbonate in an iron crucible, and the fusion leached with hot water — sodium phosphate dissolves and the carbonates of the heavy metals remain insoluble.

*b.* Another source of loss is the presence of sulphates, either in the original material or by intentional or accidental addition, in the latter case due to the oxidation of hydrogen sulphide, which has been passed into the solution during the removal of elements of the hydrogen sulphide and ammonium sulphide groups, barium and strontium sulphate being precipitated along with these members. A potassium carbonate fusion will form $K_2SO_4$, which may be leached out with water.

*c.* Loss may be caused by occlusion of barium, calcium, strontium, and magnesium by the gelatinous precipitates $Fe(OH)_3$,$Al(OH)_3$, etc. A double precipitation of these compounds should be made if considerable amounts are present.

*d.* A large excess of ammonium salts, which accumulate during the preliminary separations, will prevent precipitation of the alkaline earths. This can be avoided by using the necessary care required for accurate work, the addition of reagents by means of burettes or accord-

ing to definite measurements in graduates, etc. Careless addition of large amounts of ammonium hydroxide and hydrochloric acid should be guarded against. In case large amounts of ammonium chloride are present, time is frequently saved by a repetition of the separations. Ammonium chloride may be expelled by heating the material, taken to dryness in a large platinum dish, the ammonium salts being volatilized.

*e.* Carbon dioxide absorbed by ammonium hydroxide from the air will precipitate the alkaline earths with the ammonium sulphide group.

**Direct Precipitation on Original Sample.** — For the determination of barium, calcium, and strontium, it is advisable to take a fresh sample, rather than one that has been previously employed for the estimation of the hydrogen sulphide and ammonium sulphide groups, as is evident from the statements made above. The alkaline earths are isolated by being converted to the insoluble sulphates and separations effected as given later under Sulphate Method.

**Separation from Members of Previous Groups.** — The members of the previous groups may be removed by precipitation as sulphides by $H_2S$ passed into the acid and then the alkaline solutions, the combined filtrates concentrated to about 300 cc. and made slightly acid with hydrochloric acid. The following procedures for isolation of barium from magnesium and the alkalies and from members of the alkaline earth group may be necessary before precipitation in its final form. The methods of separation will apply to the analyses of the elements mentioned so that the details of procedure will not be given elsewhere.

**Separation of the Alkaline Earths from Magnesium and the Alkalies.** — Two general procedures will cover conditions commonly met with in analytical work:

**A. Oxalate Method.** — Applicable in presence of comparatively large portions of calcium. The acid solution containing not over 1 gram of the mixed oxides is brought to a volume of 350 cc. and for every 0.1 gram of magnesium present about 1 gram of ammonium chloride is added, unless already present. Sufficient oxalic acid is added to completely precipitate the barium, calcium, and strontium.[1] ($H_2C_2O_4.2H_2O$ = 126.04, Ba = 137.37, Ca = 40.07, Sr = 87.63.) The solution is slowly neutralized by addition, drop by drop, of dilute ammonium hydroxide (1:10), methyl orange being used as indicator. About $\frac{1}{2}$ gram of oxalic acid is now added in excess, the solution again made alkaline with ammonium hydroxide, and allowed to settle for at least two hours. The precipitate is filtered off and washed with water containing 1% ammonium oxalate, faintly alkaline with ammonia.

The precipitate contains all the calcium and practically all of the barium and strontium. If Mg is present in amounts of 10 to 15 times that of the alkaline earths a double precipitation is necessary, to re-

[1] Ca and Sr will precipitate slowly in the oxalic acid solution. Ba will precipitate on making the solution alkaline.

move it completely from this group. The oxalates are dissolved in hydrochloric acid and reprecipitated with ammonium oxalate in alkaline solution.

The filtrate contains magnesium and the alkalies. Traces of barium and strontium may be present. If the sample contains a comparatively large proportion of barium and strontium, the filtrate is evaporated to dryness, the ammonium salts expelled by gentle ignition of the residue, and the Ba and Sr recovered as sulphates according to the method described below. Magnesium is precipitated as magnesium ammonium phosphate from the filtrate.

The oxalates of barium, calcium, and strontium are ignited to oxides, in which form they may be readily converted to chlorides by dissolving in hydrochloric acid, or to nitrates by nitric acid.

**B. Sulphate Method.** — Applicable in presence of comparatively large proportions of barium, strontium, or magnesium. The solution containing the alkaline earths, magnesium and the alkalies is evaporated to dryness and about 5 cc. concentrated sulphuric acid added, followed by 50 cc. of 95% alcohol. The sulphates[1] of barium, calcium, and strontium are allowed to settle, and then filtered onto a medium mesh ashless filter paper and washed with alcohol until free of magnesium sulphate. In presence of large amounts of magnesium as in case of analyses of Epsom salts and other magnesium salts it will be necessary to extract the precipitate by adding a small amount of water, then sufficient 95% alcohol to make the solution contain 50% alcohol and filter from the residue. Magnesium is determined in the filtrate.

The residue containing barium, calcium, and strontium as sulphate is fused with 10 parts of potassium carbonate or sodium acid carbonate until the fusion becomes a clear molten mass, a deep platinum crucible being used for the fusion. A platinum wire is inserted and the mass allowed to solidify. The fusion may be removed by again heating until it begins to melt around the surface next to the crucible, when it may be lifted out on the wire. The mass is extracted with hot water and filtered, $Na_2SO_4$ going into the solution and the carbonates of barium, strontium, and calcium remaining insoluble. The carbonates should dissolve completely in hydrochloric acid or nitric acid, otherwise the decomposition has not been complete, and a second fusion of this insoluble residue will be necessary.

**Separation of the Alkaline Earths from One Another.** — This separation may be effected by either of the following processes:

1. Barium is separated in acetic acid solution as a chromate from strontium and calcium; strontium is separated as a nitrate from calcium in ether-alcohol or amyl alcohol.

[1] Solubility of $BaSO_4$ = 0.17 milligram, $CaSO_4$ = 179 milligram, $SrSO_4$ = 11.4 milligrams per 100 cc. sol. cold.

2. The three nitrates are treated with ether-alcohol in which barium and strontium nitrates are insoluble and calcium dissolves; the barium is now separated from strontium by ammonium chromate.

**Procedures: 1. (a) Separation of Barium from Strontium (and from Calcium).** — In presence of an excess of ammonium chromate, barium is precipitated from solutions, slightly acid with acetic acid, as barium chromate (appreciably soluble in presence of much free acetic acid), whereas strontium and calcium remain in solution.

The mixed oxides or carbonates are dissolved in the least amount of dilute hydrochloric acid and the excess of acid expelled by evaporation to near dryness. The residue is taken up in about 300 cc. of water and 5–6 drops of acetic acid (sp.gr. 1.065) together with sufficient ammonium acetate (30% solution) to neutralize any free mineral acid present. The solution is heated and an excess of ammonium chromate (10% neutral sol.) added (10 cc. usually sufficient). The precipitate of barium chromate is allowed to settle for an hour and filtered off on a small filter and washed with water containing ammonium chromate until free of soluble strontium and calcium (test — addition of $NH_4OH$ and $(NH_4)_2CO_3$ produces no cloudiness), and then with water until practically free of ammonium chromate (e.g., only slight reddish brown color with silver nitrate solution).

To separate any occluded precipitate of strontium or calcium the filter paper is pierced and the precipitate rinsed into a beaker with warm dilute nitric acid (sp.gr. 1.20) (2 cc. usually are sufficient). The solution is diluted to about 200 cc. and boiled. About 5 cc. of ammonium acetate, or enough to neutralize the free $HNO_3$, are added to the hot solution and then sufficient ammonium chromate to neutralize the free acetic acid, 10 cc. usually sufficient. The washing, as above indicated, is repeated. Barium is completely precipitated and may be determined either as a chromate or a sulphate or by a volumetric procedure. Strontium and calcium are in the filtrates and may be separated as follows:

**(b) Separation of Strontium from Calcium.** — The method depends upon the insolubility of strontium nitrate and the solubility of calcium nitrate in a mixture of ether-alcohol, 1:1.

Solubility of $Sr(NO_3)_2$ = 1 part $Sr(NO_3)_2$ in 60,000 parts of the mixture. Ca easily soluble.

If the solution is a filtrate from barium, 1 cc. of nitric acid is added and the solution heated and made alkaline with ammonium hydroxide followed immediately with ammonium carbonate, the carbonates of strontium (together with some $SrCrO_4$) and calcium will precipitate. The precipitate is dissolved in hydrochloric acid and reprecipitated from a hot solution with ammonium hydroxide and ammonium carbonate. The precipitate, $SrCO_3$ and $CaCO_3$, is washed once with hot water and is then dissolved in the least amount of nitric acid, washed into a small casserole, evaporated to dryness and heated for an hour at 140 to 160° C. in an oven, or at 110° C. over

night. The dry mass is pulverized and mixed with 10 cc. of ether-alcohol (absolute alcohol, one part, ether-anhydrous, one part). Several extractions are thus made, the extracts being decanted off into a flask. The residue is again dried in an oven at 140 to 160° C., then pulverized and washed into the flask with the ether-alcohol mixture and digested for several hours with frequent shaking of the flask. The residue is washed onto a filter moistened with ether-alcohol mixture. Strontium nitrate, $Sr(NO_3)_2$, remains insoluble, and may be dissolved in water and determined gravimetrically as a sulphate, oxide, or carbonate or volumetrically. Calcium is in the filtrate and may be determined gravimetrically as an oxide or volumetrically.

Instead of using a mixture of ether-alcohol, amyl alcohol may be used (hood), the mixture being kept at boiling temperature to dehydrate the alcohol to prevent solution of strontium (*b.p.* = 130° C.).

**2. Separation of Barium and Strontium from Calcium.** The procedure depends upon the insolubility of barium nitrate, $(BaNO_3)_2$, and strontium nitrate, $Sr(NO_3)_2$, in a mixture of anhydrous ether and absolute alcohol or anydrous amyl alcohol, whereas $Ca(NO_3)_2$ dissolves.

The mixed oxides or carbonates are dissolved in nitric acid and taken to dryness in a beaker or Erlenmeyer flask, and heated for an hour or more in an oven at 140 to 160° C. Upon cooling, the mixture is treated with ten times its weight of ether-alcohol mixture and digested, cold, in the covered beaker or corked flask for about two hours with frequent stirring. An equal volume of ether is now added and the digestion continued for several hours longer. The residue is washed by decantation with ether and alcohol mixture until calcium is removed (test — no residue on platinum foil with drop of filtrate evaporated to dryness).

**Separation of Barium from Strontium.** The dry mixed chlorides are dissolved in the least possible amount of water (0.2 cc., or more if necessary) the solution warmed, then cooled. More water is added if crystals appear. (The solution should be saturated.) A mixture of 4:1 HCl (33%) and ether is added dropwise with stirring. Sufficient reagent is added to precipitate $BaCl_2$ and dissolve $SrCl_2$. The mixture is decanted on an asbestos filter and washed with the HCl-ether reagent. The $BaCl_2$ is dried at 150° C. and weighed. (Method of Gooch and Soderman.)

Barium and strontium may be separated by precipitation of barium as a chromate, the nitrate residue being dissolved in water and barium precipitated according to directions given under Procedure No. 1.

Amyl alcohol may be used in place of ether-alcohol by digesting the nitrates in a boiling solution (130° C.), calcium going into solution and barium and strontium remaining insoluble as nitrates.

## METHODS FOR DETERMINING BARIUM

### GRAVIMETRIC METHODS FOR THE DETERMINATION OF BARIUM

For reasons given under "Preliminary Considerations," it is advisable to take a special sample for the determination of barium that has not undergone treatment with hydrogen sulphide or ammonium hydroxide, since these may cause the loss of barium as stated. Lead should be removed if present.

### DETERMINATION OF BARIUM BY PRECIPITATION AS SULPHATE, $BaSO_4$

This method depends on the insolubility of barium sulphate in water and in very dilute hydrochloric or sulphuric acid, one gram of the salt requiring about 344,000 cc. of hot water to effect solution.

Reaction: — $BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$.

$BaSO_4$, Mol.wt., 233.44; sp.gr., 4.47 and 4.33; m.p., 1580 degrees, (amorphous decomposes); water dissolves 0.000172 gram and 0.000334 per 100 cc. 3% HCl dissolves 0.0036 gram. Soluble in conc. $H_2SO_4$, White, Rhombic, and amorphous forms.

Reagent: Dilute sulphuric acid — one volume of strong sulphuric acid diluted by pouring into ten volumes of water. 1 cc. of this reagent contains approximately 0.145 gram of $H_2SO_4$. This is equivalent to

$$\frac{Ba}{H_2SO_4} = \frac{137.37}{98.09} \times 0.145 = \text{app. } 0.25 \text{ gram Ba per cc.}$$

**Solution.** — Soluble Barium Salts — Weigh about 1 gram of the salt in a watch glass, transfer to a beaker, 400-500 cc., and dissolve in about 250 cc. of water, add 1 cc. HCl and heat to near boiling.

*Note.* If the factor weight $\frac{Ba}{BaSO_4} = \frac{137.37}{233.44} = 0.5885$ g. is taken exactly, the final weight of barium sulphate $\times$ 100 equals per cent barium.

**Barium in Ores and Water insoluble Compounds.** — Prepare the solution under the suitable method given under "Preparation and Solution of the Sample."

Calculate the amount of the sulphuric acid reagent that is necessary to precipitate the barium in the sample, with about 20% excess. If there is no conception of the amount present add 5 cc. of the acid per gram of the sample taken, according to the following method:

1. **Precipitation.** — To the hot barium chloride solution, prepared as directed, add very slowly the calculated amount of hot dilute sulphuric acid. This may be done by means of a pipette, the acid being added in a fine stream, stirring the solution during the addition.

2. Cover the beaker and allow the precipitate to settle a few minutes then test the clear supernatant solution with a few more drops of the acid. If additional precipitate forms add 1–2 cc. more of the reagent. When the precipitation is complete, place the covered solution on the steam bath or over a low flame and allow to " digest " for at least twenty minutes. This forms larger crystals and lessens chances of loss of the barium sulphate by the precipitate passing through the filter.

3. **Filtration.** — Fit closely a fine grained " ashless " filter paper into a long stemmed funnel and moisten it with hot water to close the pores of the paper. Decant the clear solution above the precipitate into the filter, pouring the liquid down a stirring rod, with rounded end, so held as to direct the stream against the side of the filter. The stem of the funnel should rest against the side of the beaker to prevent splattering.

4. Wash the precipitate in the beaker about 4 or 5 times, adding 5–10 cc. of hot water at a time, allowing the precipitate to settle and decanting the wash water through the filter.

5. Transfer the precipitate to the filter by tilting the beaker and directing a fine stream of wash water from the wash bottle onto the sulphate, guiding it into the filter by means of the glass rod, which may be held on top of the beaker by means of the forefinger. " Cop " out the beaker by means of a rubber tipped glass rod (policeman), and wash out the beaker into the filter.

6. Wash the precipitate in the filter 3 or 4 times, or until the wash water passing through is free of sulphates. ($BaCl_2$) test. Pinch the top of the filter together and fold over. Place the filter and its contents into a weighed porcelain (or platinum) crucible, with the apex of the filter directed upward. This avoids splattering of the precipitate during drying.

7. **Ignition.** — Place the covered crucible over a low flame, until all of the moisture has been expelled. Now remove the lid and gradually increase the heat and ignite until all the carbon of the filter has been oxidized and the material in the crucible is white.

8. Cool in a desiccator. Weigh as $BaSO_4$. Convert to the equivalent Ba.

$$\frac{Ba}{BaSO_4} = \frac{137.37}{233.44} = 0.5884.$$ = the conversion factor of $BaSO_4$ to Ba.

(Weight of precipitate $\times$ 0.5884 $\times$ 100) $\div$ weight of sample = per cent barium in the sample.

Other factors: $BaSO_4 \times 0.6569 = BaO$, or $\times 0.8455 = BaCO_3$.

## DETERMINATION OF BARIUM AS A CHROMATE

A preliminary spectroscopic test has indicated whether a separation from calcium and strontium is necessary. If these are present, barium is separated along with strontium from calcium as the nitrate in presence of alcohol-ether mixture, according to directions given under "Separations." Barium is now precipitated as the chromate, $BaCrO_4$, from a neutral or slightly acetic acid solution, strontium remaining in solution.

**Precipitation of Barium Chromate.** — If barium is present in the form of nitrate, together with strontium, the mixed nitrates are evaporated to dryness and then taken up with water. About 10 cc. ammonium acetate (300 grams $NH_4C_2H_3O_2$ neutralized with $NH_4OH + H_2O$ to make up to 1000 cc.) added and the solution heated to boiling. Five cc. of 20% ammonium bichromate are added drop by drop with constant stirring and the precipitate allowed to settle until cold. The solution is decanted off from the precipitate through a filter and washed by decantation with dilute (0.5%) solution of ammonium acetate, until the excess chromate is removed, as indicated by the filtrate passing through uncolored. If much strontium was originally present, a double precipitation is necessary, otherwise the precipitate may be filtered directly into a Gooch crucible and ignited, the following paragraph directions being omitted.

**Purification from Strontium.** — The precipitate is dissolved from the filter by running through dilute (1:4) warm nitric acid, poured upon the chromate, catching the solution in the beaker in which the precipitation was made; the least amount of acid necessary to accomplish this being used and the filter washed with a little warm water. Ammonium hydroxide is now added to the solution, cautiously, until a slight permanent precipitate forms and then 10 cc. of ammonium acetate solution added with constant stirring and the mixture heated to boiling. The precipitate is allowed to settle until the solution is cold and then filtered and washed by decantation as before, a Gooch crucible being used to catch the precipitate.

**Ignition.** — The precipitate is washed once with dilute alcohol, 1:10, dried at 110° C., and ignited, gently at first and then to a dull red heat until the color of the chromate is uniform. It is advisable to cover the crucible at first and then after five minutes to remove the cover.

$$BaCrO_4 \times 0.6051 = BaO. \quad BaCrO_4 \times 0.5420 = Ba.$$

NOTES. The use of sodium hydrate or acetate in place of the ammonium hydroxide and acetate is sometimes recommended, owing to the slight solubility of $BaCrO_4$ in ammonium salts, as seen by the following table, approximate figures being given:

| | |
|---|---|
| 100,000 parts of cold water dissolves | 0.38 parts $BaCrO_4$ |
| 100,000 parts of hot water dissolves | 4.35 parts $BaCrO_4$ |
| 100,000 of 0.5 % solution of $NH_4Cl$ dissolves | 4.35 parts $BaCrO_4$ |
| 100,000 of 0.5 % solution of $NH_4NO_3$ dissolves | 2.22 parts $BaCrO_4$ |
| 100,000 of 0.75 % solution of $NH_4C_2H_3O_2$ dissolves | 2.00 parts $BaCrO_4$ |
| 100,000 of 1.5 % solution of $NH_4C_2H_3O_2$ dissolves | 4.12 parts $BaCrO_4$ |
| 100,000 of 1 % acetic acid dissolves | 20.73 parts $BaCrO_4$ |

Although the solvent action of ammonium salts is practically negligible under conditions of analysis given above, the solvent action of free acetic acid is of importance, so that it is necessary to neutralize or eliminate free mineral acids before addition of the acetate salt.

The edges of the $BaCrO_4$ precipitate upon drying may appear green, owing to the action of alcohol; upon ignition, however, the yellow chromate is obtained. The color orange yellow, when hot, fades to a light canary yellow upon cooling.

$BaCrO_4$, *mol.wt.*, 253.47; *sp.gr.*, $4.498^{15°}$; 100 cc. $H_2O$ sol. cold will dissolve $0.00038^{18°}$ gram, hot dissolves 0.0043 gram; soluble in HCl, $HNO_3$, yellow rhombic plates.

## VOLUMETRIC METHODS

### TITRATION OF THE BARIUM SALT WITH DICHROMATE

This method is of value for an approximation of the amount of barium present in a solution that may also contain calcium, strontium, and magnesium or the alkalies. It depends upon the reaction

$$2BaCl_2 + K_2Cr_2O_7 + H_2O = 2BaCrO_4 + 2KCl + 2HCl$$

N/10 $K_2Cr_2O_7$ (precipitation purposes) contains 7.355 grams pure salt per liter.

**Procedure.** — The solution containing the barium is treated with ammonia until it just smells of it. (If an excess of ammonia is present the solution is made faintly acid with acetic acid.) It is then heated to about 70° C. and the standard dichromate added, with stirring until all the barium is precipitated and the clear supernatant solution is a faint yellow color from the slight excess of the reagent. For accurate work it is advisable to titrate the precipitate formed by one of the methods given below. One cc. $K_2Cr_2O_7$ = 0.00687 gram Ba. (Note reaction given above.)

NOTE. An excess of potassium dichromate may be added, the precipitate filtered off, washed and the excess of dichromate determined as stated below.

### REDUCTION OF THE CHROMATE WITH FERROUS SALT AND TITRATION WITH PERMANGANATE

Ferrous sulphate reacts with barium chromate as follows:

$$2BaCrO_4 + 6FeSO_4 + 8H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 2BaSO_4 + 8H_2O.$$

An excess of ferrous salt solution is added and the excess determined by titration with N/10 $KMnO_4$ solution. Fe = $\frac{1}{3}$Ba.

**Reagents.** — N/10 solution of $KMnO_4$. N/10 $FeSO_4$ (27.81 grams per liter) or $FeSO_4.(NH_4)_2SO_4$ (39.226 grams per liter.) One cc. = 0.004579 Ba.

**Procedure.** — The well-washed precipitate of barium chromate is dissolved in an excess of standard N/10 ferrous ammonium sulphate solution containing free sulphuric acid. The excess ferrous salt is titrated with standard N/10 potassium permanganate solution. (Cc. N/10 ferrous solution minus cc. permanganate titration) multiplied by 0.004579 gives grams barium in the solution. Iron factor to barium is 0.8187.

### POTASSIUM IODIDE METHOD

The procedure depends upon the reactions:

1. $2BaCrO_4+6KI+16HCl=2BaCl_2+2CrCl_3+6KCl+8H_2O+6I.$
2. $3I_2+6Na_2S_2O_3=6NaI+3Na_2S_4O_6.$

**Procedure.** — The precipitate, $BaCrO_4$, is dissolved in 50 to 100 cc. of dilute hydrochloric acid and about 2 grams of solid potassium iodide salt added and allowed to react about ten minutes. The liberated iodine is now titrated with N/10 thiosulphate. Near the end of the titration starch solution is added and followed by N/10 thiosulphate until the color disappears.

One cc. N/10 $Na_2S_2O_3$ = 0.004579 gram Ba.[1]

[1] ie. $\frac{1}{3}$ mol. wt. ÷ 10,000.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### ANALYSIS OF BARYTES AND WITHERITE

Barytes or heavy spar is a variety of native barium sulphate, and witherite a native barium carbonate. These minerals are typical examples of barium-bearing ores. The analysis may involve the determination of barium and calcium sulphates or carbonates, magnesia, iron and aluminum oxides and moisture. Traces of lead, copper, and zinc may be present, as well as sulphide, sulphur and fluorine in fluorspar. The following is an approximate composition of a high-grade sample:

$BaSO_4 = 96\%$, $CaCO_3 = 1.5\%$, $MgCO_3 = 0.3\%$, $SiO_2 = 0.5\%$, $Al_2O_3 = 0.5\%$, $Fe_2O_3 = 0.2\%$, $H_2O = 0.5\%$.

For complete analysis treat as directed under preparation of the sample.

#### Procedure for Commercial Valuation of the Ore

**Total BaO as Barium Sulphate.** — One gram of the finely pulverized sample is weighed into a platinum crucible (35 cc. capacity), mixed with 8 grams of sodium carbonate, fused for twenty minutes over a Bunsen burner and twenty minutes over a Meeker burner or blast lamp. The fusion is leached out with 200 cc. hot water in a 250 cc. beaker, the barium carbonate filtered off, washed thoroughly with hot dilute sodium carbonate solution (2 grams per liter) until no test for sulphate is obtained. The barium carbonate is dissolved from the paper with hot dilute hydrochloric acid, catching solution in a 600 cc. beaker and the paper thoroughly washed. The solution is neutralized with ammonium hydroxide, made slightly acid with hydrochloric acid (1–1.5 cc.), heated to boiling and the barium precipitated with hot ammonium sulphate solution (30 grams per liter). After standing on a steam plate for four hours, the barium sulphate is filtered off on a weighed platinum Gooch crucible, ignited for 35 minutes and weighed.

*Sulphate.* — The filtrate containing the $SO_3$ and washings from the barium carbonate is acidified with hydrochloric acid, 1–1.5 cc. excess, heated to boiling, the sulphates precipitated with hot 10% barium chloride solution and proceed as above.

*Silica.* — This is determined by acidifying the extract from the barium carbonate obtained above, evaporating to dryness and taking up with water. $SiO_2$ remains insoluble. See chapter on Silicon.

*Iron and Alumina.* — Determine in filtrate from silica determination, all the barium having been removed. Precipitate as hydroxides by addition of ammonium hydroxide.

*Lime.* — Precipitate as oxalate from iron and alumina filtrate.

*Magnesia.* — Precipitate as magnesium ammonium phosphate from the filtrate of the lime determination.

*Carbon Dioxide.* — Determine as in limestone. See chapter on Carbon.

*Fluorine.* — See chapter on Fluorine.

*Loss on Ignition.* — Determine on 1 gram sample. Moisture obtained by drying at 110° C., the loss by igniting over blast.

For further details consult Standard Methods of Chemical Analysis — Scott. D. Van Nostrand Co. Pub.

## BISMUTH

**Bi, at.wt. 208.0; sp.gr. 9.7474; m.p. 271°; b.p. 1420° C.; oxides, $Bi_2O_3$, $B_2O_5$**

The determination of bismuth is required in complete analysis of ores of cobalt, nickel, copper, silver, lead, and tin, in which it is generally found in small quantities; in evaluation of bismuthite, bismuth ochre, etc., in the analysis of the minerals wolfram, molybdenite. It is determined in the residues from the refining of lead (the principal source of bismuth in the United States); in the analysis of alloys — antifriction metals, electric fuses, solders, stereotype metals, certain amalgams used for silvering mirrors (with or without lead or tin), and in bismuth compounds.

### OCCURRENCE

Bismuth is found both free and combined in nature.

*Minerals.* — The more important minerals are the following — *Native Bismuth*, Bi, is a reddish silver-white mineral with metallic lustre; sometimes in crystallized form but more commonly in granular masses, appears with branching lines in the gangue or with isolated grains; brittle; opaque; silver-white streak; hardness 2–2.5.

*Bismuthinite*, $Bi_2S_3$, a lead-gray mineral, often with yellow tarnish; metallic lustre; opaque; gray streak; sectile and brittle; hardness 2–2.5.

*Bismite, Bismuth Ochre*, $Bi_2O_3$, earthy mineral with dull or vitreous lustre; white, yellow or green color; opaque; streak colorless to greenish; hardness 2.

*Bismutite*, $Bi_2O_3.CO_2.H_2O$, an earthy white to yellow mineral; opaque, with dull or vitreous lustre; streak colorless to greenish; brittle; hardness 4–4.5. Fuses on charcoal O.F. with yellow coat, with R.F. a metallic globule of Bi obtained, which volatilizes.

### DETECTION

The solution is obtained by digesting the sample in nitric acid or by fusing with acid potassium sulphate.

Bismuth is precipitated from its solution, containing free acid, by $H_2S$ gas, as a brown sulphide, $Bi_2S_3$. The compound is insoluble in ammonium sulphide (separation from arsenic, antimony, and tin), but dissolves in hot dilute nitric acid (separation from mercury). The nitrate, treated with sulphuric acid and taken to $SO_3$ fumes, is converted to the sulphate and dissolves upon dilution with water

(lead remains insoluble as $PbSO_4$). Bismuth is precipitated from this solution by addition of ammonium hydroxide, white $Bi(OH)_3$ being formed (copper and cadmium dissolve). If this hydroxide is dissolved with hydrochloric acid and then diluted with a large volume of water, the white, basic salt of bismuth oxychloride, BiOCl, is precipitated. The compound dissolves if sufficient hydrochloric acid is present. It is insoluble in tartaric acid (distinction from antimony).

**Reducing Agents.** — Formaldehyde in alkaline solution, hypophosphorous acid, potassium or sodium stannite, reduce bismuth compounds to the metallic state. For example, a hot solution of sodium stannite poured onto the white precipitate of $Bi(OH)_3$ on the filter will give a black stain. The test is very delicate and enables the detection of small amounts of the compound.

$$3K_2SnO_2 + 2BiCl_3 + 6KOH = 2Bi + 3K_2SnO_3 + 6KCl + 3H_2O.$$

**Blowpipe Test.** — A compound of bismuth heated on charcoal with a powdered mixture of carbon, potassium iodide and sulphur, will give a scarlet incrustation on the charcoal.

## GRAVIMETRIC METHODS FOR THE DETERMINATION OF BISMUTH

### Preparation and Solution of the Sample

In dissolving the substance, the following facts must be kept in mind: nitric acid is the best solvent of the metal. Although it is soluble in hot sulphuric acid, it is only very slightly soluble in the cold acid. The metal is practically insoluble in hydrochloric acid, but readily dissolves in nitrohydrochloric acid. The hydroxides, oxides, and most of the bismuth salts are readily soluble in hydrochloric, nitric, and sulphuric acids.

**Ores or Cinders.** — One gram of the finely pulverized ore or cinder (or larger amounts where the bismuth content is very low) is treated in a 400 cc. beaker with 5 cc. of bromine solution ($Br + KBr + H_2O$) followed by the cautious addition of about 15 cc. of $HNO_3$ (sp.gr. 1.42). When the violent action has ceased, which is apt to occur in sulphide ores, the mixture is taken to dryness on the steam bath, 10 cc. of strong HCl and 20 cc. of concentrated $H_2SO_4$ and the covered sample heated until $SO_3$ fumes are freely evolved. The cooled solution is diluted with 50 cc. of water and gently heated until only a white or light gray residue remains. The solution is filtered and the residue washed with dilute $H_2SO_4$ (1:10), to remove any adhering bismuth. Silica, the greater part of the lead (also $BaSO_4$) remain in the residue, whereas the bismuth, together with iron, alumina, copper, antimony, etc., are in the solution. Details of further treatment of the solution to effect a separation of bismuth are given under "Separations" and the procedures for determination of bismuth.

**Alloys, Bearing Metal, etc.** — One gram of the borings, placed in a small beaker, is dissolved by adding 20 cc. of concentrated HCl and 5 cc. of strong $HNO_3$. The alloy will usually dissolve in the cold, unless considerable lead is present, in which case prolonged heating on the steam bath may be necessary. (A yellow or greenish-yellow color at this stage indicates the presence of copper.) Lead may now be removed either as a sulphate by taking to $SO_3$ fumes with $H_2SO_4$ or by precipitating as a chloride, in the presence of alcohol, according to directions given under Separations. The bismuth is determined in the filtrate from lead according to one of the procedures given under the quantitative methods.

**Lead Bullion, Refined Lead.** — See method outlined under "Industrial Products and Raw Materials."

*The following procedures are given in the order that would be followed in the complete analysis of an ore, in which all the constituents are sought. This general scheme, however, is not required for the majority of bismuth-bearing samples commonly met with in the commercial laboratory, direct precipitations of bismuth frequently being possible.*

**Separation of Bismuth from Members of Subsequent Groups, Fe, Cr, Al, Mn, Co, Ni, Zn, Mg, the Alkaline Earths and Alkalies, together with Rare Elements of these Groups.** — The solution should contain 5 to 7 cc. of concentrated hydrochloric acid (sp.gr. 1.19) for every 100 cc. of the sample. The elements of the hydrogen sulphide group are precipitated by saturating the solution with $H_2S$ (Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Mo, Se, Te, Au, Pt). The members of subsequent groups remain in solution and pass into the filtrate.

**Separation of Bismuth from Arsenic, Antimony, Tin, Molybdenum, Tellurium, Selenium.** — In presence of mercury, the soluble members of the hydrogen sulphide group are separated from the insoluble sulphides by digesting the precipitate above obtained with ammonium sulphide; in absence of mercury, however, which is generally the case, digestion of the sulphides with sodium hydroxide and sodium sulphide solution is preferred, the general procedure being followed. Mercury, lead, bismuth, copper, and cadmium remain in the residue, whereas the other members of the group dissolve.

**Separation of Bismuth from Mercury.** — The insoluble sulphides, remaining from the above treatment with ammonium sulphide after being washed free of the soluble members of this group, are placed in a porcelain dish and boiled with dilute nitric acid (sp.gr. 1.2 to 1.3). The solution thus obtained is filtered, upon dilution, from the insoluble sulphide of mercury. A little of the lead may remain as $PbSO_4$, the solution may contain lead, bismuth, copper, and cadmium.

**Separation of Bismuth from Lead.** — This is the most important procedure in the determination of bismuth as the separation is almost invariably necessary, as these elements commonly occur together. Bismuth produced in the United States in 1912 was obtained entirely from the residues in the refining of lead.

There are two methods for the separation of lead and bismuth.

*A.* Precipitation of lead either as lead sulphate or as lead chloride, the bismuth remaining in solution under the conditions of the precipitation.

*B.* Precipitation of bismuth as the oxychloride or subnitrate, lead remaining in solution.

**Precipitating Lead as $PbSO_4$.** — This procedure is generally used in the process of a complete analysis of an ore containing lead and bismuth. The nitric acid solution of the sulphides, obtained upon removal of the soluble group and mercury by boiling the insoluble sulphides with dilute nitric acid, is treated with about 10 cc. of strong sulphuric acid, and taken to $SO_3$ fumes by heating. The cooled sulphate solution is diluted with water and the insoluble lead sulphate filtered off and washed with dilute sulphuric acid solution (1 : 20). Bismuth passes into solution, together with copper and cadmium, if also present in the original sample.

**Separation of Bismuth from Copper and Cadmium.** — See oxychloride method, separation of bismuth as BiOCl.

## DETERMINATION OF BISMUTH AS THE OXIDE, $Bi_2O_3$

**Preliminary Considerations.** — The determination of bismuth as the oxide requires the absence of hydrochloric acid or sulphuric acid from the solution of the element, since either of these acids invariably contaminates the final product. In presence of these acids, which is frequently the case, determination of bismuth by precipitation as $Bi_2S_3$ or by reduction to the metal and so weighing is generally recommended; a brief outline of the methods is given later; a solution of bismuth free from hydrochloric acid and practically free of sulphuric acid may be obtained by precipitating $Bi_2S_3$, together with CuS, CdS, and PbS, the amount of sulphuric acid formed by the reaction being negligible. Bismuth should be in a nitric acid solution, free from antimony and tin.

Two general conditions will be considered: 1. Solutions containing lead. Copper and cadmium may also be present. 2. Solutions free from lead. Copper and cadmium may be present.

**1. Separation from Lead, Copper, and Cadmium, by Precipitation as Basic Nitrate.** — Either the sulphuric or hydrochloric acid methods may be employed for effecting the separation of lead by precipitation. Furthermore advantage may be taken of the fact that bismuth nitrate is changed by the action of water into an insoluble basic salt, while lead, copper and cadmium do not undergo such a transformation.

**Procedure.** — The bismuth nitrate solution is evaporated to syrupy consistency and hot water added with constant stirring with a glass rod. The solution is again evaporated to dryness, and the hot-water treatment repeated. Four such evaporations are generally sufficient to convert the bismuth nitrate completely into the basic salt; when this stage is reached the addition of water will fail to produce a turbidity. The solution is finally evaporated to dryness and, when free from nitric acid, is extracted with cold ammonium nitrate solution ($1\ NH_4NO_3 : 500\ H_2O$) to dissolve out the lead and other impurities. After allowing to stand some time with frequent stirring, the solution is filtered and the residue washed with ammonium nitrate solution, then dried.

**Ignition to Bismuth Oxide.** — As much of the precipitate as possible is transferred to a weighed porcelain crucible, the filter is burned and the ash added to the main precipitate. This is now gently ignited over a Bunsen burner. Too high heating will cause the oxide to fuse and attack the glaze of the crucible.

**Properties.** — $Bi(OH)_2NO_3$ *mol.wt.*, 304.03; *sp.gr.*, $4.928^{15°}$; *decomp.*, 260°; *insol. in* $H_2O$; *sol. in acids*; *hexagonal plates.*

$Bi_2O_3$ *mol. wt.*, 464.0; *sp.gr.*, 8.8 *to* 9.0; *m.p.*, 820 to 860°; *insoluble in cold water and in alkalies, but soluble in acids*; *yellow tetragonal crystals.*

$$Bi_2O_3 \times 0.8965 = Bi.$$

**2. Precipitation of Bismuth as the Subcarbonate or Hydroxide, Lead being Absent.** — Either of these procedures effects a separation of bismuth from copper and cadmium.

**A. Procedure. Precipitation of the Subcarbonate.** — The solution is diluted to about 300 cc. and dilute ammonia added cautiously until a faint turbidity is obtained and then an excess of ammonium carbonate. The solution is heated to boiling, the precipitate filtered off, washed with hot water, dried and ignited according to directions given in the bismuth subnitrate method. The residue is weighed as $Bi_2O_3$.

**B. Procedure. Isolation of Bismuth by Precipitation as the Hydroxide.** — The solution is taken to dryness and the residue treated with 5 cc. of nitric acid (1 : 4) and 25 cc. of water added. The resulting solution is poured, with constant stirring, into 25 cc. of concentrated ammonia and 50 cc. of 4% hydrogen peroxide. Upon settling of the bismuth hydroxide, the clear solution is filtered off and the residue is treated with more ammonia and peroxide. It is then filtered onto a filter paper, washed with hot, dilute ammonium hydroxide, (1 : 8), followed by hot water and washed free of any adhering copper or cadmium (no residue when a drop is evaporated on platinum foil). Re-solution in hot dilute nitric acid and reprecipitation may sometimes be necessary to obtain the pure product. The hydroxide may be dried, ignited and weighed as $Bi_2O_3$ according to directions already given on page 135.

**Properties.** — $Bi_2O_3.CO_2.H_2O$, *mol. wt.*, 526.02; *sp.gr.*, 6.86; *decomp. by heat; insoluble in water, soluble in acids, insoluble in* $Na_2CO_3$; *white precipitate.*

$Bi(OH)_3$, *mol. wt.*, 259.02; *loses* $1\frac{1}{2}$ $H_2O$ *at* 150°; *insol. in cold water and in alkalies; soluble in acids; white precipitate.*

## DETERMINING BISMUTH BY PRECIPITATION AND WEIGHING AS THE BASIC CHLORIDE, BiOCl

The determination depends upon the formation of the insoluble oxychloride, BiOCl, when a hydrochloric acid solution of bismuth is sufficiently diluted with water, the following reaction taking place, $BiCl_3 + H_2O = BiOCl + 2HCl$.

The procedure is recommended for the determination of bismuth in refined lead, bearing metal, and bismuth alloys. Copper, cadmium, and lead do not interfere; appreciable amounts of antimony and tin, however, should be removed by $H_2S$ precipitation and subsequent treatment with $Na_2S$, and the residual sulphides dissolved in hot dilute nitric acid, according to directions given under "Separations."

*Properties of* BiOCl. *Mol.wt.*, 259.46; *sp.gr.*, $7.717^{15°}$; *m.p.*, red heat; *insol. in* $H_2O$ *and in* $H_2C_4H_4O_6$, *soluble in acids. Appearance is white, quadratic crystalline form.*

**Procedure.** — The solution of bismuth, freed from appreciable amounts of tin and antimony, is warmed gently and treated with

sufficient ammonia to neutralize the greater part of the free acid. At this stage a precipitate is formed by the addition, which dissolves with difficulty; the last portion of the dilute ammonia (1 : 2) is added drop by drop, the solution is diluted to about 300 cc., and the remainder of the free acid neutralized with dilute ammonia added cautiously until a faint opalescence appears, but not enough to form an appreciable precipitate. One to 3 cc. of dilute hydrochloric acid (1 part HCl sp.gr. 1.19 to 3 parts $H_2O$) are now added, the mixture stirred and the bismuth oxychloride allowed to settle for an hour or so on the steam bath, then filtered hot by decanting off the clear solution through a weighed Gooch crucible. The precipitate is washed by decantation twice with hot water and finally washed into the Gooch, then dried at 100° C. and weighed as BiOCl.

$$BiOCl \times 0.8017 = Bi.$$

Note. Three cc. of dilute hydrochloric acid (or 1 cc. conc. HCl, sp.gr. 1.19) are sufficient to completely precipitate 1 gram of bismuth from solution.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### BISMUTH DETERMINATION IN LEAD BULLION [1]

Ten to twenty-five grams of the lead, hammered or rolled out and cut into small pieces, are taken for analysis. The sample is dissolved in a mixture of 200 cc. of water and 50 cc. of strong nitric acid, in a large covered beaker, and warmed gently on water or steam bath. When lead has dissolved, the beaker is removed and placed on a cool surface and enough sulphuric acid (1–1) added to precipitate lead.

The lead sulphate is allowed to settle and the clear supernatant liquid is decanted into another beaker and held. To the residue of lead sulphate 10–20 cc. of concentrated sulphuric acid is added and brought down to strong fumes on a hot plate. After strong fuming, the portion containing lead sulphate is diluted with water. To the first clear decanted portion, 10 cc. of sulphuric acid is added and this also evaporated down to fumes of sulphuric acid. Both portions are removed from the hot plate and when cool add 50 cc. of water and 3 to 5 grams of tartaric acid to each. Heat to dissolve tartaric acid and filter over an asbestos pad, the clear portion first, and then follow with the one containing the bulk of lead sulphate. The bulk of lead sulphate is washed by decantation three or four times with warm water before transferring to an asbestos pad. When bismuth is higher than .30% in the bullion, the sulphate residue may be retreated with sulphuric acid, fumed and washed. The clear solution is allowed to stand for one hour and refiltered to ensure removal of all lead sulphate. The filtrate is then warmed and hydrogen sulphide gas passed, filtered on a paper and washed with cold $H_2S$ water. The sulphides are washed from the filter back to the precipitating beaker. The sulphides of Sb, Sn, Te, etc., are leached out with a 10% $K_2S$ solution, which has been saturated with hydrogen sulphide, and allowed to stand in a warm place and filtered over the original sulphide paper. After washing with warm water containing a few drops of $K_2S$ solution, the precipitate is dissolved in nitric acid and a few drops of bromine to ensure solution of all sulphur. It is all important to remove Sb, Sn and Te from the sulphide precipitate before going any further by repeating the hydrogen sulphide precipitation.

The nitric acid solution of Bi, Cu, etc., is made faintly alkaline with ammonia and 1 gram of ammonium carbonate added and the solution boiled for five to ten minutes when the bismuth is precipitated as a basic salt. To ensure solution of the copper, a few drops of free ammonia are added with stirring before filtering. The bismuth pre-

[1] J. J. Mulligan.

cipitate is filtered on a tared gooch, washed with water, dried and ignited to $Bi_2O_3$ over a Bunsen flame.

$$Bi_2O_3 \times .8966 = Bi.$$

If the bismuth precipitate is dark after precipitation with ammonia and ammonium carbonate, it may be due to tellurium. If so, the filtered precipitate is dried, ignited and fused with caustic potash and sulphur to put the tellurium in a soluble form and thus remove tellurium from insoluble bismuth sulphide; or redissolving in acid and reprecipitating as sulphides and washing the sulphides with $K_2S$ solution as before mentioned.

This method is applicable to refined lead when larger portions are taken.

## BISMUTH IN ALLOYS

The alloy is dissolved in nitric acid, adding as little hydrochloric as possible, and 10 cc. of sulphuric, and run down to strong $SO_3$ fumes and proceed as for ores.

Where bismuth is present with considerable tin, the cementation of the bismuth with pure iron wire to free it from tin and then treating residue same as for ores and mattes, seems to be the best means for obtaining a bismuth precipitation free of tin for control analyses.

In the presence of considerable copper, the bismuth can be precipitated as basic carbonate, filtered and the impure basic precipitate treated with nitric acid and evaporated to fumes of sulphuric; the procedure is then the same as for ores and matte.

## DETERMINATION OF BISMUTH IN ORES, MATTES

A qualitative test for lead and insoluble bismuth compounds on all products to be analyzed for bismuth is an important step with the removal of lead as sulphate as soon as perfect solution of the sample is insured.

For products containing from $\frac{1}{2}\%$ to 25% bismuth, one gram portions are taken; for 50% or higher $\frac{1}{2}$ gram portions are weighed up.

The weighed portion is transferred to a 250 cc. beaker and 25 cc. of $H_2O$ and 10 cc. of concentrated nitric acid added, and where sulphur is present a few drops of bromine are added cautiously after the acid has been allowed to act for a sufficient time. After all sulphur has gone into solution, boil down to dryness on the water bath or hot plate, 2 cc. of nitric acid and 1 cc. of hydrochloric acid are added, then 10 cc. of sulphuric acid cautiously added, and the cover sample taken down on the hot plate to strong fumes of $SO_3$. The cooled solution is diluted with 50 cc. of water and 2 to 3 grams of tartaric acid are added and the mixture brought to a boil. The residue, containing insoluble lead sulphate and silica or insoluble matter, is filtered and washed with 2% solution of sulphuric acid to free residue of soluble bismuth.

The filtrate contains Bi, Cu, Sb, As, Te and a small amount of Pb may be in the solution. After standing for one-half hour or more, the solution is refiltered to remove any lead that may have gone through on the first filtration.

The clear solution containing bismuth is saturated with hydrogen sulphide gas for one-half hour.

Filter sulphides on filter paper and wash with $H_2S$ water. If much iron is present the sulphides are redissolved in nitric and sulphuric acids taken to fumes, and the sulphide precipitation repeated.

[1] J. J. Mulligan.

The sulphides are leached with a 10% solution of $K_2S$ saturated with $H_2S$ gas to remove As, Sb, Sn, Te and Se. The remaining sulphides containing Cu, Cd, Bi are dissolved in nitric acid and a little bromine water, bromine boiled off and the solution made slightly alkaline with ammonia water and 1 gram of ammonium carbonate added. The solution is boiled for five to ten minutes and 1 cc. of ammonia is added and the basic carbonate filtered on a tared Gooch, ignited and weighed as $Bi_2O_3$.

$$Bi_2O_3 \times .8966 = Bi.$$

### CINCHONINE POTASSIUM IODIDE, COLORIMETRIC METHOD

This method is applicable for the determination of small amounts of bismuth, 0.00003 to 0.00015 gram, in ores and alloys. The procedure depends upon the fact that bismuth nitrate produces a crimson or orange color when its solution is added to a solution of cinchonine potassium iodide, the intensity of the color depending upon the amount of bismuth in the resulting product.

**Special Reagents. Cinchonine Potassium Iodide Solution.** — Ten grams of cinchonine are dissolved by treating with the least amount of nitric acid that is necessary to form a viscous mass and taking up with about 100 cc. of water. The acid is added a drop at a time, as an excess must be avoided. Twenty grams of potassium iodide are dissolved separately and cinchonine solution added. The resulting mixture is diluted with water to 1000 cc. The reagent should be filtered free of suspended matter before use.

**Standard Bismuth Solution.** — One gram of metallic bismuth is dissolved in the least amount of dilute nitric acid (1:1) that is necessary to keep it in solution and diluted to 1000 cc., in a graduated flask. One hundred cc. of this solution is diluted to 1000 cc. One cc. contains 0.0001 gram bismuth.

**Procedure. Isolation of Bismuth.** — The solution is freed from lead by $H_2SO_4$, and from arsenic, antimony, and tin by precipitation of the sulphides and extraction with $Na_2S$ solution. The residual sulphides are dissolved in hot dilute nitric acid, according to the standard methods of procedure. The free nitric acid is nearly neutralized by the cautious addition of dilute ammonia, the last portion being added drop by drop, until a faint cloudiness is evident, and then 10 to 15 cc. of 10% ammonium carbonate are added with constant stirring. The mixture is digested for about three hours on the steam bath, the clear solution decanted through a small filter, the residue washed by decantation once or twice with hot water containing ammonium carbonate and then on the filter twice with pure hot water.

**Colorimetric Comparison.** — The residue of bismuth basic carbonate is dissolved in the least amount of dilute nitric acid necessary to effect solution and the filter washed free of bismuth with a little water containing a few drops of nitric acid. The solution is made up to a definite volume, 50 cc. or 100 cc. according to the bulk of precipitate dissolved. Two small beakers placed side by side may be used for the color comparison, a sheet of white paper or tile being placed under the beakers. Two 50-cc. Nessler tubes, however, are preferred. Three cc. of cinchonine solution are added to each container. From a burette the bismuth nitrate sample is run into one of these containers in just sufficient quantity to color the reagent a crimson or orange tint. The exact volume required to do this is noted and the equivalent amount of sample used calculated. (If no color is produced bismuth is absent.) The reagent in the adjacent beaker or Nessler tube is diluted to 5 to 7 cc., and into this is run, from a burette, the standard bismuth nitrate solution until the color exactly matches the sample. From the cc. of the standard required the amount of bismuth in the sample can readily be calculated.

**Reaction.** $3KI + C_{19}H_{22}N_2OKI + Bi(NO_3)_3 = C_{19}H_{22}N_2OKIBiI_3 + 3KNO_3$.

**Precautions.** — The sensitiveness of the method is lost if the depth of color is too great. It is necessary, then, to add the sample to the cinchonine reagent in such quantity only as will produce a light crimson or orange color.

## BORON

**B, at.wt. 11.0;** { **amorp. sp.gr. 2.45; m.p. 2200° C.; b.p. sublimes.**
**cryst. sp.gr. 2.55; m.p. 2500° C.; b.p. 3500° C.; oxide, $B_2O_3$.**

The determination of boron is required in the valuation of its minerals. The determination is required for obtaining the true value of commercial boric acid, in the analysis of fluxes and certain pigments. It is determined as a food-preservative in milk, meat, canned goods, etc. The element is determined in certain alloys of nickel, cobalt, zinc, chromium, tungsten, molybdenum and in the analysis of steel.

### OCCURRENCE

The element occurs in nature in the form of boric acid and its salts (" borates ").

*Minerals.* — *Borax*, $Na_2B_4O_7.10H_2O$, occurring as a glistening white efflorescence of certain soils, frequently in solution in lakes. The crystals are monoclinic, vitreous to dull lustre; translucent to opaque; color white, gray, blueish or greenish; taste alkaline; brittle; white streak; hardness 2–2.5.

*Colemanite*, $Ca_2B_6O_{11}.5H_2O$, occurs in groups of transparent monoclinic crystals; vitreous to dull lustre; transparent to opaque; white streak; hardness 4–4.5.

*Ulexite, Boronatrocalcite*, $CaNaB_5O_9.8H_2O$ — White rounded masses or loosely-compacted, intertwined silky fibres; translucent; brittle; white streak; hardness 1, easily pulverized between the fingers.

*Other Minerals.* — *Danburite*, $CaB_2(SiO_4)_2$; *Datolite*, $HCaBSiO_5$; *Axinite*, Ca, Al boro silicate; *Tourmaline*, complex boro silicate.

### DETECTION

**Flame Test.** — Boric acid is displaced from its salts by nearly all acids, including even carbonic acid.

The flame test may be conveniently made by treating the powdered sample in a test-tube with sulphuric acid and alcohol (preferably methyl alcohol). A cork carrying a glass tube is inserted and the test-tube gently warmed. The escaping gas will burn with a green flame.

**Borax Bead.** — $Na_2B_4O_7.10H_2O$ fused in a platinum loop, swells to several times its orignial volume as the water of crystallization is being driven out, then contracts to a clear molten bead. If the bead is

dipped into a weak solution of cobalt and plunged into the flame, until it again becomes molten, the bead upon cooling will be colored blue.

**Turmeric Test.** — A few drops of acetic acid are added together with 2 or 3 drops of an alcoholic turmeric solution to an alcoholic extract of the sample, placed in a porcelain dish. The solution is diluted with water and then evaporated to dryness on the water bath. 1/1000 milligram of boric acid will produce a distinct color, 2/100 milligram will give a strong reddish-brown colored residue, which becomes bluish-black when treated with a drop of sodium hydroxide solution.

## GRAVIMETRIC DETERMINATION OF BORON

Analysis of Industrial Products and Raw Materials. The solubility of boron compounds prevents complete precipitation by any of the known reagents, hence most of the gravimetric methods are indirect.

### DISTILLATION AS METHYL BORATE AND FIXATION BY LIME[1]

This excellent method, originally worked out by F. A. Gooch,[1] and later modified by Gooch and Jones, depends upon the fact that the borates of alkaline earths and alkalies give up their boron in the form of the volatile methyl borate (*b.p.*, 65° C.), when they are distilled with absolute methyl alcohol (acetone-free). The methyl borate passed over lime in presence of water is completely saponified, the liberated boric acid combining with the lime to form calcium borate, which may be dried, ignited, and weighed. The increase of the weight of the lime represents the $B_2O_3$ in the sample.

$$2B(OCH_3)_3 + CaO + 6H_2O = 6CH_3OH + Ca(BO_2)_2 + 3H_2O.$$

**Procedure. Preparation of the Sample.** — It will be recalled that crystalline boron is scarcely attacked by acids or alkaline solutions; the amorphous form, however, is soluble in concentrated nitric and sulphuric acids. Both forms fused with potassium hydroxide are converted to potassium metaborate. Boric acid is more readily soluble in pure water than in hydrochloric, nitric, sulphuric, or acetic acids, but still more soluble in tartaric acid.[2] It is soluble in alcohol and volatile oils. Borax is insoluble in alcohol. With acids it becomes transposed to boric acid and the sodium salt of the acid.

**Boric Oxide in Ores, Silicates, Enamel, etc.** — About 0.5 gram of the finely ground material is fused with five times its weight of sodium carbonate, the melt extracted with water and the extract, containing the sodium salt of boric acid, evaporated to small volume. The greater part of the excess sodium carbonate is neutralized with hydrochloric acid and finally made acid with acetic acid (litmus paper test = red). Boric oxide is now determined by the distillation process.

About 1 gram of pure calcium oxide is ignited to constant weight over a blast lamp and then transferred to the dry Erlenmeyer receiving flask (Fig. 47). The crucible in which the lime was heated and weighed is set aside in a desiccator for later use.

0.2 gram or less of the alkali borates, obtained in solution by the procedure given under " Preparation of the Sample," is treated with a

[1] Proc. Am. Acad. of Arts and Sciences, **22**, 167–176 (1886).
[2] (Herz, Chem. Zentr., 1903, 1, 312).

few drops of litmus (or lacmoid), solution and the free alkali neutralized with dilute HCl solution added drop by drop. A drop of dilute sodium hydroxide solution is added and then a few drops of acetic acid. The slightly acid solution is transferred to the pipette-shaped retort *R*, Fig. 47, by means of the attached funnel *F*, washing out the beaker and funnel with three 2 to 3 cc. portions of water. The stopcock of the funnel is closed, the apparatus is connected up as shown in the illustration, the paraffine bath, heated to not over 140° C., placed in position and the liquid in the retort distilled into the receiver containing the known amount of lime. When all the liquid has distilled over, the paraffine bath is lowered, the retort allowed to cool for a few minutes, 10 cc. of methyl alcohol (acetone-free) added to the residue in *R* and the contents again distilled by replacing the paraffine bath. The process is repeated three times with methyl alcohol.

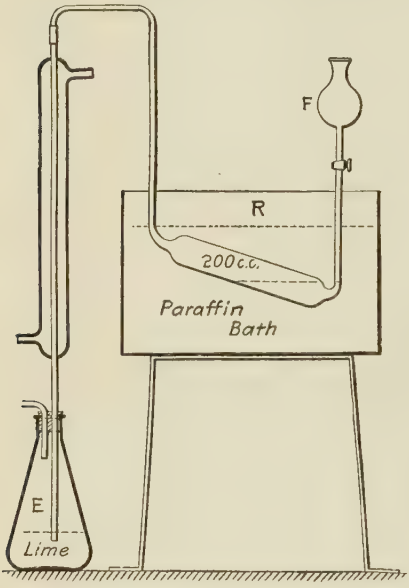


FIG. 47. Distillation of Methyl Borate

The contents of the retort (which are now alkaline), are made distinctly acid by addition of acetic acid, and three more distillations made with 100 cc. portions of methyl alcohol, as before. The paraffine bath is now removed, the receiving flask is stoppered, the contents thoroughly mixed by shaking, and set aside for an hour or more for complete saponification of the methyl borate. The contents are now poured into a large platinum dish and evaporated on the water bath at a temperature below the boiling-point of the alcohol. (Loss of boric acid will occur if the alcohol boils.) The adhering lime in the receiving flask is dissolved by wetting its entire surface with a few drops of dilute nitric acid (the flask being inclined and revolved to flow the acid over its sides). The contents are transferred to the dish with a little water and the evaporation repeated. No loss of boric acid will take place at this stage, the alcohol having been removed during the first evaporation. The residue is gently heated to destroy any calcium acetate that may have formed, the cooled borate and lime are taken up with a little water and transferred to the crucible in which the lime was heated and weighed. The material clinging to the dish is dissolved with a little nitric acid (or acetic acid), and washed into the

crucible. The contents of the crucible are evaporated to dryness on the water bath, then heated very gently over a flame (the crucible being covered) and finally more strongly. The heating is continued

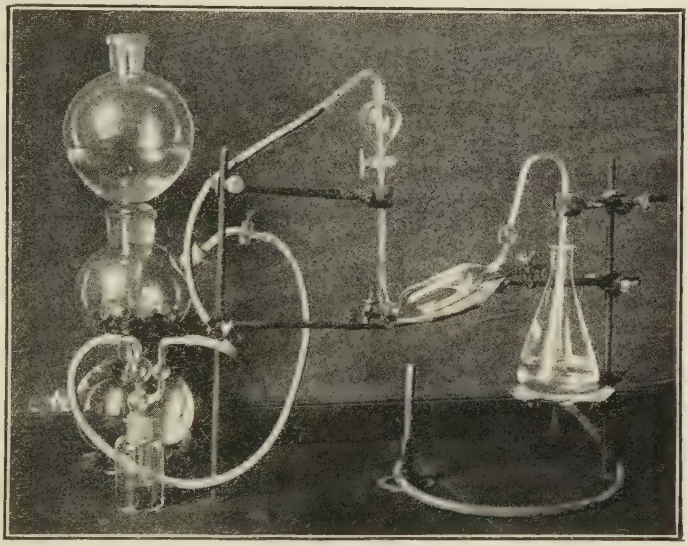


FIG. 47*b*

until a constant weight is obtained. The increase of weight of the lime represents the amount of $B_2O_3$ in the sample.

NOTES. Gooch and Jones worked out a procedure which utilizes sodium tungstate as a retainer of the methyl borate, in place of the lime. This substance is definite in weight, not hydroscopic, soluble in water, and recoverable in its original weight after evaporation and ignition. "Methods in Chem. Anal.," p. 204, 1st Ed. By F. A. Gooch, John Wiley & Sons, Publishers.

The receiving flask has a cork stopper with a hole to accommodate the tube of the condenser and a slit to permit the escape of air from the flask.

Gooch recommends cooling of the receiving flask.

## VOLUMETRIC DETERMINATION OF BORON

### Titration of Boric Acid in Presence of Mannitol or Glycerol Evaluation of Borax

The method takes advantage of the fact that boric acid reacts neutral to methyl orange (or paranitrophenol), but is acid to phenolphthalein, and may be quantitatively titrated in the presence of mannitol or of glycerol, which prevent the hydrolization of sodium borate. If insufficient mannitol or glycerol are present the color change takes place too soon, the color fading upon adding more of these substances. The end-point is reached when the further addition of these reagents produces no fading of the color. In the procedure, the alkali is neutralized in presence of methyl orange (or paranitrophenol), and the liberated boric acid is now titrated.

**Reactions.** $Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$
$H_3BO_3 + NaOH = NaBO_2 + 2H_2O.$

**Borax, Boric Acid.** — Ten grams of the material are dissolved in about 300 cc. of water (free from $CO_2$) and made to 500 cc. in a graduated flask, with pure water. One hundred-cc. portions are taken for analysis and the solution titrated, in presence of mannitol or glycerol according to directions given under the volumetric procedure.

### Method of Chapin [1]

**Reagents Required:**

1. *Paranitrophenol.* — One gram dissolved in 75 cc. of neutral ethyl alcohol and made up to 100 cc. with water.
2. *Phenolphthalein.* — One gram dissolved in 100 cc. of ethyl alcohol and made up to 200 cc. with water.
3. *Hydrochloric Acid, 0.1 Normal.* — The water should be boiled to remove carbonic acid.
4. *Hydrochloric Acid, 1.1 Strength.* — A dropping bulb should be filled with this acid when it is needed in accurate small amounts.
5. *Sodium Hydroxide, 0.5 and 0.1 Normal.* — These should be standardized as follows: Fuse pure boric acid in a platinum dish. While still warm break the melt up and place the fragments quickly in a weighing tube. Dissolve 1.75 grams in 250 cc. of hot, recently boiled water, cool, and dilute the solution to 500 cc. This solution is 0.1 normal — that is, in presence of mannite or glycerol 1 cc. is neutralized to the phenolphthalein end point by 1 cc. of 0.1 normal sodium hydroxide.

In standardizing the sodium hydroxide against this solution both indicators should be used, so that the end may be the same as that

[1] Bulletin 700, "The Analysis of Silicate and Carbonate Rocks," by W. F. Hillebrand. Department of the Interior, U. S. Geological Surveys.

seen in actual titration. Follow exactly the directions given under *b*, below, for the final titration, only assuming that the boric acid solution is exactly neutral to paranitrophenol — that is, free from mineral acid. When sodium hydroxide is standardized in this way the small amount of carbonate present does no harm.

6. *Mannite.* — This is preferable to glycerol, for it requires no special preparation, does not materially increase the bulk of the solution to be titrated, and gives an equally sharp end point.

7. *Methyl Alcohol.* — This should be distilled over lime after it has been heated for some hours in contact with the lime under a reflux condenser. The more nearly anhydrous the alcohol is the better.

8. *Calcium Chloride.* — This should be granular, anhydrous, and free from boron.

### Apparatus

The main set up of the apparatus required is shown in Fig. 48.

**Procedure.** — Take half a gram of mineral powder for even very small amounts of boron. When the percentage is high it is best to so limit the weight of the sample so that the $B_2O_3$ shall not exceed 0.1 gram.

If the mineral is soluble in hydrochloric acid, transfer 1 gram of it to the flask *B*, without letting any adhere to the neck, and treat with not more than 5 cc. of 1:1 hydrochloric acid. Heat gently on a water bath until solubility is complete.

If the mineral is not soluble, add to it exactly six times its weight of sodium carbonate or of an equimolecular mixture of sodium and potassium carbonates, mix, and fuse in the usual manner. Without removing from the crucible, decompose the melt with 1:1 hydrochloric acid in calculated amount added by degrees. While this is being done the crucible should rest in a casserole, and the lid should be kept in place as much as possible. Toward the end it may be necessary to heat a little, but care should be taken not to boil, for boric acid would be lost with the steam. Pour the solution into the flask *B* and rinse the crucible with a very little water. See Fig. 48.

Then add pure anhydrous calcium chloride, using about 1 gram for each cubic centimeter of solution and running it through a paper funnel to keep the neck of the flask clean. Twirl the flask a little to allow the chloride to take up the water, connect it with the rest of the apparatus, raise the casserole beneath it until the flask rests in the water but does not touch the bottom, and then begin the distillation of the alcohol from the flask *A*, taking care that the open end of the capillary "boiling tube" is free from alcohol and that the U tube attached to the receiver is trapped with water.

The decomposition flask, *B*, is not heated until about 25 cc. of alcohol has condensed in it. After that the water bath is heated by a small flame and the flask thus kept hot enough to prevent further

condensation of alcohol. The distillation should not be so rapid as to permit escape of methyl borate from the system.

When a distillate of about 100 cc. has collected the receiver is exchanged for a fresh one and the collection of a second distillate is

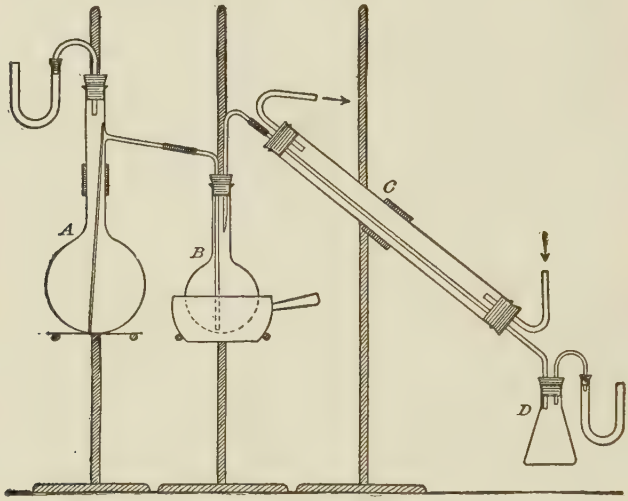



FIG. 48. Distilling Apparatus for Boron

*A*. Flask of 500 cc. capacity for methyl alcohol, having a U tube containing a little mercury as a safety trap, and a capillary " boiling tube " 3 mm. in bore, the bore closed at 1 cm. from the lower end.

*B*. Flask of 250 cc. capacity, supported, in a casserole of water but not touching the bottom. The outlet tube of *B* should be not less than 12 cm. in vertical height and of rather wide bore. The end inside the flask should be jagged to allow condensed liquid to drop back instead of jumping up the tube.

*C*. Glass condenser, 40 cc. long, of tubing 3 cm. wide.

*D*. Receiving flask of 250 cc. capacity. Two or three of these flasks should be at hand, with necks of same size, so that the receiver can be changed without interrupting the distillation. The small U tube attached contains a little water to prevent the escape of any uncondensed methyl borate.

*E*. (Not shown.) A second glass condenser like *C*, connected on the one side to a flask exactly like *B*, which, however, has a stopper with only one hole and rests completely within a large bath. The flask carries also a " boiling tube." On the other side is a receiver like *D*, but without the U trap. This apparatus is used for distilling off the alcohol after the preliminary titration.

*F*. (Not shown.) Filter pump. At the end of the side tube is an elbow tube connected to a rubber stopper with two holes and of a size to fit the flask mentioned in connection with *E*. The second hole of the stopper is closed by a glass plug, which can be withdrawn to break the vacuum. Midway between pump and stopper is a small safety bottle, to prevent the tap water from sucking back into the flask.

proceeded with. The contents of the trap tube are added to the first receiver, and a preliminary titration is made as follows: Add a few drops of paranitrophenol solution and run in the standard sodium hydroxide until the indicator shows that the free mineral acid is

neutralized. Next, add 1 cc. of the phenolphthalein solution and continue the titration until the color of that indicator begins to appear. The end point will not be sharp, but the amount of alkali used between the two end points indicates approximately the amount of boric acid in the distillate. If the mineral is likely to contain more than 3 or 4% of $B_2O_3$ use 0.5 normal solution, the object being to keep the distillate as free from the water as possible and thus facilitate the dehydration later on.

After completing the titration add to the distillate twice as much alkali as was used between the two end points, transfer the distillate to the second distilling apparatus, and boil off the alcohol. The addition of the indicated amount of alkali prevents loss of boron by converting unstable $NaBO_2$ to stable $Na_3BO_3$.

In the meantime the second distillate of 100 cc. will have collected. Unless the alcohol contained water or insufficient calcium chloride was used, this second distillate will contain the remainder of the boron. Therefore, before removing the receiver stop the distillation. Treat the second distillate exactly like the first and then add it to the first.

If the amount of alkali used for titrating the second distillate is less than 0.1 cc. of the 0.1 normal solution the distillation may be regarded as complete.

When the liquid from which the alcohol is being distilled no longer boils in the steam bath, remove it to a casserole, rinsing the flask once or twice with water, and heat over a direct flame, rotating the casserole while doing so, until the little remaining alcohol has been boiled out. The residue should now be small — about 25 cc. if 0.1 normal alkali was used and much less if 0.5. If the volume is less than 25 cc. make up to that extent.

Return the solution to the flask and add drop by drop with constant twirling 1 : 1 hydrochloric acid from a dropping bulb, until the color of both indicators is discharged, taking care not to add a drop too much. Now put in the "boiling tube," heat the flask in the steam bath for a minute or two, then attach to the filter pump and boil under reduced pressure until the liquid is nearly cold and only an occasional bubble appears.

All carbon dioxide being thus removed, break the vacuum, cool if necessary under the tap, and proceed to the final titration.

First neutralize the excess of hydrochloric acid by running in carefully 0.5 normal sodium hydroxide until the yellow of paranitrophenol just appears. Bring back to acid reaction with 0.1 normal hydrochloric acid and then to the appearance of a faint yellow with 0.1 normal alkali. The solution is now exactly neutral as the indicator itself shows this color in a neutral solution. Make sure that the end point is reached exactly. One drop of 0.1 normal acid should discharge the color entirely.

Now add 1 gram of mannite, read the burette, and continue titrating to the end point of phenolphthalein. Add another gram of man-

nite, and if this causes a disappearance of the end color add more alkali until it reappears.

The number of cubic centimeters of alkali used multiplied by its equivalent in terms of $B_2O_3$ gives the amount of the latter contained in the solution. If the solution of alkali is exactly 0.1 normal this equivalent is 0.0035.

The changes of color that take place during the titration need mention. When the mannite (or glycerol) is added to the solution the yellow color due to the paranitrophenol disappears at once. This is due to the fact that the combination of these reagents with the boric acid forms an acid of sufficient strength to affect the indicators, although boric acid alone does not. As the titration proceeds the color reappears and grows stronger, becoming very intense just before the phenolphthalein end point appears. The latter will be noticed as a faint brownish tinge, and then another drop of the 0.1 normal alkali changes it to an intense brownish red, which is the real end point.

## BROMINE

**Br, at.wt. 79.92; sp.gr. 3.1883; m.p. — 7.3° C.; b.p. 58.7° C.; acids, HBr, HBrO, $HBrO_3$**

### OCCURRENCE

Bromine is found chiefly combined with the alkalies and the alkaline earths, hence occurs in many saline springs and is a by-product of the salt industry. It is found in silician zinc ores, Chili saltpeter, in sea water (probably as $MgBr_2$), in marine plants. Traces occur in coal, hence it is found in gas liquors. Bromine never occurs free in nature.

The substance is used in metallurgy, the arts, and medicine. It is a valuable oxidizing agent for the laboratory.

### DETECTION

The product is dissolved in water and tested.

**Silver Nitrate** solution precipitates silver bromide, AgBr, light yellow, from solutions containing the bromine anion. The precipitate is insoluble in dilute nitric acid, but dissolves with difficulty in ammonium hydroxide and is practically insoluble in ammonium carbonate solution (distinction from AgCl).

**Carbon Disulphide or Carbon Tetrachloride** shaken with free bromine solution, or with a bromide to which a little chlorine water has been added, (a large excess of chlorine must be avoided, as this forms BrCl compound), will absorb the bromine and become a reddish-yellow color, or if much bromine is present, a brown to brownish-black. In the latter case a smaller sample should be taken to distinguish it from iodine.

**Bromates** are first reduced by a suitable reducing agent such as cold oxalic acid, sodium nitrate, hydrochloric acid, etc., and the liberated bromine tested as directed above. *Silver nitrate* added to bromates in solution precipitates $AgBrO_3$, which is decomposed by hydrochloric acid to bromine gas.

**Barium Chloride** precipitates $Ba(BrO_3)_2$, which is reduced readily to bromine as directed above.

**Magenta Test for Bromine.** — The test reagent is made by adding 10 cc. of 0.1% solution of magenta to 100 cc. of 5% solution of sulphurous acid and allowing to stand until colorless. This is the stock solution. Twenty-five cc. of this reagent is mixed with 25 cc. of glacial acetic acid and 1 cc. of sulphuric acid. Five cc. of this is used in the test.

**Test.** — Five cc. of the magenta reagent is mixed with 1 cc. of the solution tested. Chlorine produces a yellow color. Bromine gives a reddish-violet coloration. The colored compound in each case may be taken up with chloroform or carbon tetrachloride and a colorimetric comparison made with a standard.

In halogen mixtures, iodine is first eliminated by heating with an iron per-salt. Bromine is now liberated by adding sulphuric acid and potassium chromate. A glass rod with a pendant drop of sodium hydroxide is held in the vapor to absorb bromine, and the drop then tested with the magenta reagent. After iodine and bromine are eliminated, chlorine may be tested by heating the substance with potassium permanganate, which liberates this halogen.

Note. The element is a dark, brownish-red, volatile liquid, giving off a dark reddish vapor with suffocating odor, irritating the mucous membrane (antidote dil. $NH_4OH$, ether), very corrosive. Acts violently on hydrogen, sulphur, phosphorus, arsenic, antimony, tin, the heavy metals, and on potassium, but has no action on sodium, even at 200° C. Bleaches indigo, litmus, and most organic coloring matter. It is a strong oxidizing agent. Bromine displaces iodine from its salts, but is displaced by chlorine from its combinations.

## GRAVIMETRIC METHODS

### Preparation and Solution of the Sample

The following facts regarding solubility should be remembered: The element bromine is very soluble in alcohol, ether, chloroform, carbon disulphide, carbon tetrachloride, concentrated hydrochloric acid and in potassium bromide solution. One hundred cc. of water at 0° C. is saturated with 4.17 grams of bromine, and at 50° C. with 3.49 grams. The presence of a number of salts increases its solubility in water, e.g., $BaCl_2$, $SrCl_2$, etc.

Bromides are soluble in water, with the exception of silver, mercury, lead, and cuprous bromides.

Bromates are soluble in water with the exception of barium and silver bromates and some basic bromates.

### PRECIPITATION AS SILVER BROMIDE

The general directions for determination of hydrochloric acid and chlorides apply for determining hydrobromic acid and bromides.

**I. Hydrobromic Acid and Bromides of the Alkalies and Alkaline Earths.**

**Procedure.** — The bromide in cold solution is made slightly acid with nitric acid and then silver nitrate added slowly with constant stirring until a slight excess is present. The mixture is now heated to boiling and the precipitate settled in the dark, then filtered through a weighed Gooch crucible, and washed with water containing a little nitric acid and finally with pure water to remove the nitric acid. After ignition the silver bromide is cooled and weighed as AgBr.

$$AgBr \times 0.4256 = Br, \text{ or } \times 0.6337 = KBr.$$

**II. Heavy Metals Present.**

If heavy metals are present it is not always possible to precipitate silver bromide directly. The heavy metals may be removed by precipitation with ammonia, sodium hydroxide or carbonate and the bromide then determined in the filtrate as usual.

### Notes on Separations

**Separation of Bromine from the Heavy Metals.** — Bromides of the heavy metals are transposed by boiling with sodium carbonate, the metals being precipitated as carbonates and sodium bromide remaining in solution.

**Separation of Bromine from Silver (AgBr) and from Cyanides (AgCN).** — The silver salts are heated to fusion. The mass is now treated with an excess of zinc and sulphuric acid, the metallic silver and the paracyanogen filtered off and the bromine determined in the filtrate.

## VOLUMETRIC METHODS

Free hydrobromic acid may be titrated with standard alkali exactly as is described for the determination of hydrochloric acid in the chapter on Acids. One cc. normal caustic solution is equivalent to 0.08093 gram HBr.

### DETERMINATION OF FREE BROMINE. POTASSIUM IODIDE METHOD

The method depends upon the reaction $KI + Br = KBr + I$.

**Procedure.** — A measured amount of the sample is added to an excess of potassium iodide, in a glass-stoppered bottle, holding the point of the delivering burette just above the potassium iodide solution. The stoppered bottle is then well shaken, and the liberated iodine titrated with standard thiosulphate solution.

One cc. of N/10 thiosulphate, $Na_2S_2O_3$ = 0.007992 gram Br.

### DETERMINATION OF BROMINE IN SOLUBLE BROMIDES LIBERATION OF BROMINE BY ADDITION OF FREE CHLORINE

When chlorine is added to a colorless solution of a soluble bromide, bromine is liberated, coloring the solution yellow. At boiling temperature the bromine is volatilized, the liquid becoming again colorless. When the bromide is completely decomposed and bromine expelled, further addition of chlorine produces no color reaction. $KBr + Cl = KCl + Br$.

**Procedure.** — The solution containing the bromide is heated to boiling and standard chlorine water added from a burette (protected from the light by being covered with black paper), the tip of the burette being held just above the surface of the hot bromide solution to prevent loss of chlorine. The reagent is added in small portions until finally no yellow coloration is produced. From the value per cc. of the chlorine reagent the bromine content is readily calculated.

**Standard Chlorine Water.** — The reagent is made by diluting 100 cc. of water saturated with chlorine to 500 cc. This solution is standardized against a known amount of pure potassium bromide (dried at 170° C.), the same amount of bromide being taken as is supposed to be present in the solution examined. The value per cc. of the reagent is thus established.

### SILVER–THIOCYANATE–FERRIC ALUM METHOD. (VOLHARD)

The procedure is the same as that used for the determination of chlorine. The bromide solution is treated with an excess of tenth-normal silver nitrate solution, and the excess of this reagent determined by titration with ammonium thiocyanate, using ferric alum indicator. One cc. of the thiocyanate should be equivalent to 1 cc. of silver nitrate solution. The formation of the red ferric thiocyanate indicates the completed reaction. Consult the procedure in the chapter on Chlorine.

One cc. of N/10 $AgNO_3$ = 0.007992 gram Br.

## CADMIUM

**Cd, at.wt. 112.4; sp.gr. 8.642; m.p. 320.9° C; b.p. 778° C.; oxide CdO.**

### OCCURRENCE

Cadmium occurs in small quantities in practically all zinc ores and is found in most spelters and commercial zinc materials as sheet zinc, zinc oxide, etc. In ores it occurs usually as the sulphide; the rare mineral greenockite being CdS. The metal cadmium is largely obtained as a by-product from zinc smelting. It is used in certain alloys, as trial plates for silver coinage and more recently in substitutes for tin base-bearing metals. Precipitated yellow cadmium sulphide is used as a paint pigment. Some dental amalgams contain cadmium.

Cadmium is determined, after separation from other elements, by weighing as the sulphide or as the metal following electrolysis. As it usually occurs in small quantities in the presence of large quantities of zinc, several precipitations with hydrogen sulphide are necessary and the methods must be followed in close detail to obtain accurate results. The determination of cadmium is necessary in case of spelters sold under specified rejection limits, in ores purchased and to be smelted for such spelter, and in other zinciferous material where cadmium is deleterious to the finished product. The methods to be used for the determination of cadmium in spelter is given under the chapter on zinc.

**Minerals.** — The element occurs in the rare minerals *Greenockite*, CdS; *Cadmiumoxide*, CdO; *Octavite*, Cadmium carbonate.

### DETECTION

The sample is best dissolved in aqua regia. When the violent action has subsided about 5 cc. of sulphuric acid are added and the nitric acid expelled by evaporation to small volume until white fumes of sulphuric acid appear. Water is now added and tests made on the solution obtained.

**Hydrogen Sulphide Test.** — Cadmium is detected in the *wet way* by precipitation as the yellow sulphide by hydrogen sulphide from an acid solution. It is distinguished from arsenic, antimony and tin (stannic) by the insolubility of its sulphide in ammonium hydroxide or colorless ammonium sulphide; from tin (stannous) by its insolubility in yellow ammonium sulphide; and from mercury by its solubility in hot nitric acid.

**Spectrum.** — Brilliant Green and Blue Lines.

**Blowpipe Tests.** Heated on charcoal in the reducing flame, cadmium gives a brown incrustation which is volatile.

The detection of cadmium may be made in the *dry way* through the tube test. This test is carried out in the following manner. A piece of hard glass tubing of about 5 mm. bore is sealed at one end. From 200–400 milligrams of the fine dried ore is mixed with a reducing agent as dry powdered charcoal and introduced into the tube.[1] The tube is heated just above the mixture of ore and reducing agent and drawn out to a capillary of about 1 mm. diameter. The end of the

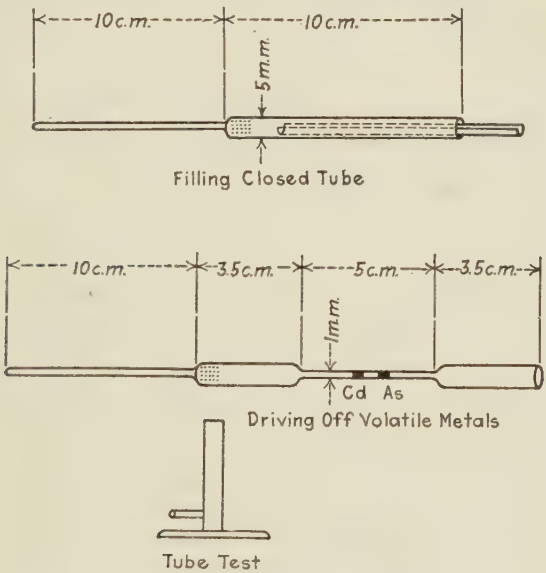



Fig. 49

tube containing the mixture is now heated in the blast lamp and the cadmium together with zinc, arsenic, antimony, etc., is volatilized and condensed in the capillary in the form of separated rings. The cadmium ring is detected from the others by introducing a little powdered sulphur into the tube and heating so that the sulphur vapor passes over the rings. The cadmium is converted to sulphide and appears red while hot and yellow while cold. Very small amounts of cadmium may be detected in this way and it is possible with experience to estimate, from the appearance of the ring, either metallic or sulphide, the amount of cadmium present.

[1] All metals present in the ore must be in the oxidized state. Sulphide ores must be carefully roasted before using in this test. In the case of metallic substances, however, no reducing agent is necessary.

### Preparation and Solution of the Sample

Samples of metals, as spelter, cadmium metal, brass, etc., should be in the form of drillings, sawings or pourings, taken in a proper manner to be representative of the lot and of sufficient fineness to preclude against a nonrepresentative sample being weighed for analysis. The samples of ore or fine material should be ground to pass a 100-mesh screen. Metallics, if also present, are kept separate from the fine material which passes through the screen, and in weighing out the sample, proportional amounts of each are taken.

Metallic cadmium is slowly soluble in hot moderately dilute hydrochloric acid or sulphuric acid, much more readily in nitric acid. It is soluble in ammonium nitrate. The oxide is soluble in mineral acids.

**Solution of Ores.** — Details of the procedure may be found under the gravimetric methods for determining cadmium. Decomposition may be best effected by adding hydrochloric acid, allowing this to react and following this with nitric acid. Or aqua regia may be added at once.

**If lead is present** it is advisable to add 5–6 cc. of concentrated sulphuric acid after the hydrochloric-nitric acid treatment and to evaporate to fumes. After cooling, water is added and the mixture digested on the water bath until the soluble salts are in solution. Lead sulphate is filtered off and washed with dilute sulphuric acid 1 : 15. The filtrate is used for the determination of cadmium.

**Carbonates** are readily dissolved in hydrochloric acid. Evaporation to dryness is necessary, generally, to dehydrate silica and remove it from the mixture. The residue is taken up with dilute HCl in the usual way, $SiO_2$ remains insoluble and is filtered off.

**Alloys** are best dissolved in hydrochloric-nitric acid mixtures, followed by sulphuric acid. The nitric acid is expelled by evaporation to fumes and the method followed above described for separation of lead.

The separation of cadmium may be made from lead since cadmium sulphate is soluble in dilute sulphuric acid while lead sulphate is not; from bismuth since ammonium hydroxide precipitates bismuth hydroxide but holds cadmium in solution, and from copper by passing hydrogen sulphide into the solution containing potassium cyanide which prevents the precipitation of copper sulphide but not cadmium sulphide.

## GRAVIMETRIC METHODS

### DETERMINATION AS CADMIUM SULPHIDE

**Procedure for Ores.** — A 10 gram sample of the finely pulverized ore is weighed out into a 400 cc. beaker, moistened with water and 50 cc. of aqua regia carefully added. When violent action has stopped, the beaker is placed on a warm plate to complete decomposition. The cover glass and sides of beaker are washed down with water, 25 cc. of sulphuric acid (1:1) added and evaporation carried to fumes. Water (100 cc.) is added, boiled until all soluble salts are dissolved, and the residue filtered off, and washed, using suction.

A steady stream of hydrogen sulphide is passed for 30–40 minutes through the filtrate, which should have a volume of approximately 300 cc. After all iron in solution has been reduced, ammonium hydroxide is added 1 cc. at a time until a heavy precipitation of zinc sulphide has taken place.[1] The precipitate is allowed to settle, the clear solution decanted and finally the bulk of the precipitate transferred to a 15 cc. paper, and washed with cold water. The sulphides on the paper are dissolved with hydrochloric acid (1:2) catching the solution in a clean beaker. Any precipitate adhering to the sides of the original beaker is also dissolved off and poured into the filter. After all zinc sulphide has been dissolved, the paper is washed three more times with the hydrochloric acid.[2] To the solution 15 cc. of sulphuric acid are added and evaporation carried just to fumes. Water is added (200 cc.) and hydrogen sulphide passed through as before. Ammonium hydroxide should be added one drop at a time, only to start the precipitation of cadmium sulphide. This precipitate is filtered off, redissolved as previously and a third precipitation made.[3] Before making the final precipitation, the solution should be allowed to stand, and any lead sulphate filtered off. The final precipitate of cadmium sulphide is filtered on a weighed Gooch crucible.

The cadmium sulphide on the Gooch crucible need only be washed once or twice, if at all, as it usually receives sufficient washing in the transfer to the crucible, and in the scrubbing and washing out of the beaker. After drying at 110° C. for 1 hour, the crucible is cooled, weighed and the cadmium calculated from the difference in weights.

$$CdS \times .778 = Cd.$$

[1] The solution should always be sufficiently acid so that no iron, etc., precipitates.

[2] This strength of acid will leave on the paper as an insoluble residue all the As, Cu, and Hg, most of the Sb, and some of the Bi and Sn. The second precipitation of CdS should free the Cd of the rest of the Sb, but not the Bi or Sn.

[3] It is necessary to make three or even four precipitations of cadmium sulphide in order to free it completely of zinc.

NOTE. It is seldom that bismuth and tin will be encountered in making a determination for cadmium so that the procedure for removing these elements need rarely be used. Cadmium sulphide precipitated from sulphuric acid is bright yellow to orange. If the precipitate is brown in color, bismuth and tin should be looked for and removed.

A very retentive filter paper must be used for the cadmium sulphide precipitates.

In dissolving the cadmium sulphide precipitates from the filter paper, the funnel should be covered to guard against loss by spraying. The number of treatments with hydrochloric acid depends upon the amount of sulphides on the paper. The paper may be finally washed with water after all sulphides have dissolved, if desired.

It is not absolutely necessary to wash the final precipitate of cadmium sulphide on the Gooch, as this has been accomplished in the transfer of the precipitate from the beaker. This has been included in the methods to safeguard against free acid remaining on the Gooch.

## DETERMINATION AS SULPHATE

The final precipitate of cadmium sulphide is dissolved with hydrochloric acid, and evaporated to dryness in a weighed platinum crucible or dish. A slight excess of dilute sulphuric acid is poured over the residue and evaporated over a steam bath or warm plate. The excess of sulphuric acid is driven off by heating in an air bath, or in a muffle heated below a dull red heat. For an air bath, the crucible or dish may be placed in a larger vessel, and this outer vessel heated to redness. $CdSO_4 \times 0.5392 = Cd$.

## ELECTROLYTIC DETERMINATION OF CADMIUM

The final precipitate of CdS is dissolved and the cadmium determined electrolytically as given under cadmium in spelter, Chapter on Zinc, or if the amount of cadmium is large the electrolytic determination is best carried out with a potassium cyanide electrolyte. The hydrochloric acid solution of cadmium, after separation of interfering elements is taken to fumes with sulphuric acid, a drop of phenolphthalein added for indicator, and a pure solution of sodium hydroxide added until a permanent red color is obtained. A strong solution of potassium cyanide is added drop by drop until the cadmium hydroxide just dissolves, avoiding any excess. The solution is diluted to 100 cc. with water, electrolyzed cold using a gauze electrode with a current of 0.5–0.7 ampere and voltage of 4.8–5.0. At the end of 5–6 hours the current is increased to 1–1.2 amperes and electrolysis continued for an hour more. The electrode is removed from the solution the instant the current is broken and immediately washed with water, followed by alcohol and ether. After drying at 100° C., the electrode is cooled and weighed. Prolonged heating of the deposit should be avoided.

*Rapid deposition* can be effected by means of the rotating anode (600 revolutions per minute). The solution of cadmium sulphate containing 3 cc. of $H_2SO_4$ (1:10) per 150 cc. The solution, heated to boiling, is electrolyzed with a current of $N.D._{100} = 5$ amperes, E.M.F. = 8–9 volts. Fifteen minutes is sufficient for the deposition of .5 gram of cadmium.

NOTES. Before washing and discontinuing the current, it is advisable to add a little water to raise the level of the liquid and continue the electrolysis to ascertain whether the deposition is complete.

Traces of cadmium may be estimated in the above solution by saturating this with $H_2S$ and comparing the yellow-colored colloidal cadmium sulphide solution with a known quantity of cadmium and the same amounts of potassium hydroxide and cyanide as in the solution tested.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### SULPHIDE METHOD FOR CADMIUM

The determination of cadmium in spelter is best carried out by either of the two following methods, according as the amount to be determined is low or high.

#### Cadmium in Spelter (Cd. — .001% to .02%)

A sample of 500 grams is taken and placed in a 2000 cc. flask with 500 cc. of water and 100 cc. of 1:1 sulphuric acid. Sulphuric acid(1:1) is added in small quantities from time to time, to maintain solution of the zinc (but never any violent action), until about 90% of the sample has been dissolved. This requires about 750 cc. of 1:1 sulphuric acid. When the evolution of hydrogen has become slow, after the last addition of acid, the solution is filtered off, retaining as much of the undissolved metallics as possible in the flask. The metallics are washed twice with water, decanting and pouring the small amount of residue on the filter. The material on the filter is then washed from the paper into the original flask and all dissolved in nitric acid. The solution is washed into a 600 cc. beaker and sufficient sulphuric acid (1:1) added to convert all the metals present to sulphates, leaving an excess of free acid of 10–15 cc. This requires about 95 to 100 cc. of acid. The solution is evaporated until all nitric acid has been expelled.

After cooling, water is carefully added and the beaker heated until all the soluble salts have been dissolved. The lead sulphate is allowed to settle, filtered off and washed. Enough water must be added to keep all zinc sulphate in solution after cooling. Hydrogen sulphide is passed through the filtrate for 15–20 minutes. No precipitate will appear at first, so that a drop or two of ammonia is added and repeated at intervals until a considerable amount of zinc sulphide has been precipitated. The sulphides are then filtered off and washed with cold water. The film of sulphides on the side of the original beaker and the sulphides on the paper are dissolved in 1:2 hydrochloric acid, washing with water, and catching the solution in a tall 400 cc. beaker, 15 cc. of 1:1 sulphuric acid are added and evaporation carried down to fumes. After cooling, 200 cc. of water are added, hydrogen sulphide passed through and ammonia added as above to produce a precipitate of cadmium sulphide. The precipitate is treated as before and a third precipitation made. In the case of very low cadmium, a fourth precipitation is advisable. The last precipitate is filtered at once on a weighed Gooch crucible, washed with cold water, dried at 110° C. and weighed as CdS or the cadmium may be weighed as metallic cadmium, by dissolving the last precipitate and electrolyzing as given by the following method:

The last precipitation of cadmium as CdS is filtered off, washed with cold water, and dissolved in dilute hydrochloric acid as in previous precipitations, catching solution and washings in original beaker. Twenty-five cc. of 1:1 sulphuric acid are added and evaporation carried to dense fumes. After cooling, a small amount of water is added, the solution neutralized with ammonia (using methyl orange as indicator), then made just acid with sulphuric acid (sp.gr. 1.09) and 3 cc. added in excess. The solution is then transferred to a 250 cc. beaker, (washing out the original beaker), diluted to cover the cylinder (beaker $\frac{2}{3}$ full), and electrolyzed over night using a current of one ampere. The cylinder with cadmium deposit is removed, washed with water and alcohol, dried at 110° C., removed from oven as soon as dry, cooled and weighed.

### Cadmium in Spelter (Cd — 0.2% to 1.0%)

A sample of 10 (or 25) grams is taken and entirely dissolved in a tall 400 cc. beaker with nitric acid, the solution then treated with 25 (or 50) cc. of 1:1 sulphuric acid and evaporated to expel all nitric acid. After cooling, water is carefully added and the beaker heated until all the soluble salts have been dissolved. The lead sulphate is allowed to settle, filtered off and washed. The filtrate is diluted to 200 cc. and hydrogen sulphide gas passed through for 15–20 minutes. No precipitate will appear at first, so that a drop or two of ammonia is added and repeated at intervals until a considerable amount of zinc sulphide has been precipitated. The sulphides are filtered off and washed with cold water. They are then dissolved with 1:2 hydrochloric acid, catching in the original beaker, 15 cc. of 1:1 sulphuric acid added and taken to fumes. This is again diluted to 200 cc., hydrogen sulphide gas passed through, and ammonia added as before to produce a precipitate of cadmium sulphide. This is treated as above and a third precipitation made. The cadmium sulphide from this is filtered at once on a weighed Gooch, washed with cold water, dried at 110° C., and weighed as CdS, or the cadmium may be weighed as metallic cadmium, by dissolving the last precipitate and electrolyzing as given in previous method.

### Notes on Separations

**Removal of Silica.** — Evaporate with hydrochloric acid or sulphuric acid, and filter off the dehydrated silica, using suction.

**Removal of Lead.** — Evaporate to fumes with sulphuric acid, cool, take up with water, warm until all soluble salts are dissolved and allow to stand until all lead sulphate settles. By using sulphuric acid to dehydrate the silica, lead and silica may be separated together.

**Separation from Ammonium Sulphide Group, Except Zn, Alkaline Earths, and Alkalies.**— The solution from lead and silica separation containing 12 cc. of sulphuric acid (1 : 1) per 100 cc. of solution is saturated cold with hydrogen sulphide, passing a steady stream for 20–30 minutes, and after the first 5 minutes adding a drop of ammonium hydroxide until zinc sulphide precipitates in quantity. It is necessary to add ammonium hydroxide to bring down zinc in order to assure the complete precipitation of cadmium. The precipitate of sulphides is filtered off and washed with cold water.

**Removal of Arsenic, Antimony and Tin.**— The precipitate on the filter is washed with ammonium hydroxide or colorless ammonium sulphide, dissolving out the arsenic, antimony and tin (stannic). If tin in the stannous condition is found to be present, yellow ammonium sulphide must be used. Arsenious sulphide is practically insoluble in the hydrochloric acid used in dissolving the cadmium sulphide. Antimonious sulphide is also only slightly soluble, so that these sulphides remain behind in carrying out the analysis.

The sulphides of tin, however, are soluble in the hydrochloric acid and must be removed before the final precipitation of cadmium sulphide.

**Removal of Bismuth, Copper and Mercury.**— Bismuth is not removed in the course of analysis as its sulphide is soluble in hydrochloric acid and hence it must be removed by precipitating with ammonium hydroxide before the final precipitation of cadmium is made. Copper sulphide is, however, practically insoluble in the hydrochloric acid used and remains behind when dissolving the first precipitations of cadmium sulphide, so that the use of potassium cyanide need seldom be resorted to. Mercuric sulphide is practically insoluble in cold hydrochloric acid (1 : 2) and is left behind in carrying out the analysis.

**Separation from Zinc.**— Cadmium is separated from the accompanying zinc by successive precipitations with hydrogen sulphide, each time bringing down less zinc, until finally only cadmium is precipitated. In the presence of a large quantity of zinc it is not possible to precipitate all cadmium with the acidity required to prevent the precipitation of any zinc sulphide.

## CALCIUM

**Ca, at.wt. 40.07; sp.gr. 1.5446 $^{29°}$; m.p. 810° [1] C.; oxide, CaO**

The determination of calcium is required in the complete analysis of ores. It is of special importance in the analysis of mortar, cement, bleaching powder, plaster of Paris, certain paint pigments, calcium bicarbonate in water, boiler scale, etc.

### OCCURRENCE

It is estimated that 3.47 per cent of the earth's crust is made up of calcium. The element does not occur free in nature. It occurs combined in a very large number of minerals some of which are found in immense deposits. As oxalate it occurs in plant cells. It is found in nearly all mineral springs, artesian wells, and river waters, principally as bicarbonate of calcium, $CaHCO_3$. Among the more important minerals are the following:

**Minerals.**[1] — *Fluorite*, (Fluor Spar), $CaF_2$ occurs usually in glassy transparent cubes of cleavable masses, colorless but more often wine-yellow, green, violet, blue or brown or black varieties; or massive zigzag strips of different colors; brittle; streak white; hardness 4.

*Calcite*, (Limestone, Marble, Iceland Spar) $CaCO_3$. Colorless, white, pale shades of red, green and blue; transparent to opaque; vitreous to dull lustre; brittle; white streak; hardness 3. Crystals rhombohedral, cleavable, coarse, fine grained or fibrous masses.

*Dolomite*, (Pearl Spar, Magnesian Limestone), $CaCO_3.MgCO_3$, small, pearly white, pink or yellow rhombohedral crystals, with curved faces, frequently white marble with coarse or fine grain, or gray, brown or black. Translucent to opaque; brittle; white streak; hardness 3.5–4.

*Aragonite*, (Flos Ferri) $CaCO_3$, white, violet, yellow or pale green, translucent or transparent, simple or pseudohexagonal, needle-like,

[1] Other minerals. Labradorite, Oligoclase, Andesite, mixtures of $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$; Anorthite, $CaAl_2Si_2O_8$; Pyroxene, CaMg etc. silicate; Wollastonite, $CaSiO_3$; Pectolite, $HNaCa_2(SiO_3)_3$; Amphibole, Ca, Mg etc. silicate; Grossularite, $Ca_3Al_2(SiO_4)_3$; Andradite, $Ca_3Fe_2(SiO_4)_3$; Uvarovite, $Ca_3Cr_2(SiO_4)_3$; Scapolite Group, mixtures of $Ca_4Al_6Si_6O_{25}$ and $Na_4Al_3Si_9O_{24}Cl$; Vesuvianite, $Ca_8[Al(OH,F)]Al_2(SiO_4)_5$; Danburite, $CaB_2(SiO_4)_2$; Datolite, $HCaBSiO_5$; Zoisite, $Ca_2(AlOH)Al_2(SiO_4)_3$; Epidote $Ca_2[(Al.Fe)OH](Al.Fe)_2(SiO_4)_3$; Axinite, CaAl borosilicate; Prehnite, $H_2Ca_2Al_2(SiO_4)_2$; Ilvaite, $CaFe_2(FeOH)(SiO_4)_2$; Apophyllite, $H_7KCa_4(SiO_3)_8.4\ 1/2H_2O$; Heulandite, $H_4CaAl_2(SiO_3)_6.3H_2O$; Stilbite, $(Na_2Ca)H_4Al_2Si_6O_{18}.4H_2O$; Chabazite, $(CaNa_2)Al_2Si_4O_{12}.6H_2O$; Titanite, $CaTiSiO_5$; Apatite, $Ca_4(CaF)(PO_4)_3$; Colemanite, $Ca_2B_6O_{11}.5H_2O$; Glauberite, $Na_2SO_4.CaSO_4$; Scheelite, $CaWO_4$.

stalactic and coral-like crystals; white streak; brittle; hardness 3.5–4.

*Anhydrite*, $CaSO_4$, granular, sugar-like, or fibrous and lamellar masses, white, gray, bluish or red crystals; translucent to opaque; with pearly lustre; white streak; brittle; hardness 3–3.5.

*Gypsum*, $CaSO_4.2H_2O$, soft, colorless, white or tinted masses, silky transparent to opaque crystals, cleavable into plates and strips or monoclinic form; brittle, laminae flexible; white streak; hardness 1.5–2.

## DETECTION

The sample is dissolved in hydrochloric acid and the tests made on portions of the solution thus obtained, the insoluble matter being filtered off. For further preparation of the solution including the separations see Detection under Barium.

In the usual course of qualitative and quantitative analysis calcium passes into the filtrates from the elements precipitated by hydrogen sulphide in acid and alkaline solutions (Ag, Hg′, Hg″, Pb, Cu, Cd, As, Sb, Sn, Fe, Cr, Al, Mn, Ni, Co, Zn, etc.), and is precipitated from an ammoniacal solution by ammonium carbonate as calcium carbonate, along with the carbonates of barium and strontium. The separation of calcium from barium and strontium is considered under Separations. The oxalate of calcium is the least soluble of the alkaline-earth group.[1] All, however, are soluble in mineral acids. Calcium oxalate may be precipitated from weak acetic acid solution by ammonium oxalate.

**Flame Test.** — The flame of a Bunsen burner is colored yellowish red when a platinum wire containing calcium salt moistened with concentrated hydrochloric acid is held in the flame.

**Spectrum.** — An intense orange and green line with a less distinct violet line. Note chart of the spectra of the alkaline earths. Plate II.

See chapter on Barium under Preliminary Tests.

[1] Solubility: $CaC_2O_4.H_2O$ = 0.000554 gram per 100 cc. $H_2O$. $BaC_2O_4.H_2O$ = 0.0093 gram. $SrC_2O_4.H_2O$ = 0.0051 gram. $MgC_2O_4.2H_2O$ = 0.07 gram.

### Rapid Preliminary Examination for Barium, Strontium, and Calcium

Make a mixture of the chloride solutions of barium, strontium, and calcium, using about 5 cc. of each. Divide into three portions, *A*, *B*, *C*.

| *A. Calcium Sulphate test for Strontium and Barium.* | *B. Detection of Barium and Strontium in a mixture.* | *C. Detection of Calcium in a mixture of the soluble salts of the group.* |
|---|---|---|
| Add about four volumes of a saturated solution of $CaSO_4$ to portion *A*. The precipitate consists of $BaSO_4$ and $SrSO_4$. These sulphates are both less soluble than that of calcium. | Test *A* indicates the presence of strontium or barium or both. Test *B* is to detect each. Add to the solution a slight excess of $K_2CrO_4$. A yellow precipitate indicates $BaCrO_4$. Filter and add to the filtrate 2–3 cc. of a saturated solution of $CaSO_4$. A white precipitate indicates the presence of Strontium. | Add a few drops of $H_2SO_4$ as long as a precipitate forms. Filter and to the filtrate add $NH_4OH$ to alkalinity and then a solution of $(NH_4)_2C_2O_4$. A fine, white precipitate insoluble in dilute acetic acid is $CaC_2O_4$. |

### SUGGESTIONS FOR THE STUDENT

The student is referred to the gravimetric method on page 170 and the volumetric method on page 173 for the determination of calcium. Use a water soluble salt for practice and follow up with limestone or dolomite or gypsum.

## GRAVIMETRIC DETERMINATION OF CALCIUM

### PRECIPITATION OF CALCIUM OXALATE AND IGNITION TO CALCIUM OXIDE

Calcium oxalate is precipitated from feebly ammoniacal solutions or from solutions acidified with acetic, oxalic, citric, or salicylic acids, by means of ammonium oxalate. The presence of ammonium chloride hinders precipitation of magnesium and does not interfere with that of calcium. If, however, much magnesium (or sodium) is present it will contaminate the calcium precipitate so that a second precipitation is necessary to obtain a pure product. The compound formed from hot solutions is crystalline or granular and filters readily, whereas the flocculent precipitate formed in cold solutions does not. Calcium oxalate, $CaC_2O_4.H_2O$, decomposes at red heat to CaO, in which form it is weighed.

#### Solution of the Sample

**Solution of Gypsum, Plaster of Paris, Sulphates, Limestones, Dolomites, Magnesites, Cements, Lime, etc.** — One gram of the powdered material is digested in a 250 cc. beaker with 20 cc. of water, 10 cc. of concentrated hydrochloric acid, and 5 cc. of nitric acid (sp.gr. 1.42). The beaker is covered to prevent loss by effervescence. When the violent action has subsided, the sample is placed on a hot plate and boiled for a few minutes. The watch-glass is rinsed into the beaker and the solution filtered. The residue is washed, dried and ignited in a platinum crucible, and then fused with a little sodium carbonate or bicarbonate. The cooled fusion is dissolved in hot dilute hydrochloric acid, the liquid added to the main solution and calcium determined by precipitation as calcium oxalate, after removal of silica, iron, alumina, etc.

Separations. **Removal of Silica.** — The solution obtained by the above procedure is evaporated to dryness and the silica dehydrated at 110° C. for an hour. The residue is now extracted with dilute hydrochloric acid. Silica remains insoluble and may be filtered off. The solution contains lime, together with iron, alumina, magnesia, etc., as chlorides.

**Removal of Iron and Alumina.** — The filtrate from the silica residue is treated with a few drops of nitric acid and boiled to oxidize the iron. Ammonia is now added cautiously until the solution just smells of it (a large excess over that required to neutralize the acid and combine with iron and alumina, will tend to dissolve $Al(OH)_3$). The precipitated hydroxides are allowed to settle and then filtered hot through a rapid filter and washed with hot water. Calcium, together with magnesium, is in solution and passes into the filtrate.

Calcium may be precipitated in presence of iron. See procedures on page 173.

**Removal of Copper, Nickel, Cobalt, Manganese, Zinc, and Elements Precipitated as Sulphides in Acid and Alkaline Solutions.** — This separation is seldom required in lime-bearing ores. In analyses of pyrites and certain other ores, containing members of the hydrogen sulphide and ammonium sulphide groups, the removal of these impurities is necessary.

The solution from the residue of silica is made slightly ammoniacal and $H_2S$ passed into the solution to saturation (or ammonium sulphide may be added). The precipitated sulphides are filtered off from the solution heated to boiling. The filtrate containing the calcium is boiled down to 50 to 75 cc. and the precipitated sulphur removed by filtration. Calcium is determined in the filtrate by precipitation with ammonium oxalate or oxalic acid. The filtrate should contain sufficient ammonium chloride to hold magnesium in solution in presence of ammonium oxalate.

1. *General Procedure.* — The following method is applicable to substances commonly examined for calcium. Decomposition having been effected by treating the material with HCl, $HNO_3$, $H_2SO_4$ and taking to fumes (accomplished quickly in a flask over a direct flame), the cooled mass is treated with about 5 cc. HCl and 100 cc. of water. Lead will be largely thrown out as $PbSO_4$, silicon as $SiO_2$. A few drops (1 cc.) $K_2Cr_2O_7$ (saturated solution) are added to insure the precipitation of lead, 25 cc. of Br water are added and just sufficient ammonia to make the solution ammoniacal. The solution is boiled for about 5 minutes, Mn, Fe, Al are precipitated. The combined precipitates are now filtered off.

Note. If much Mn is evident by a dark colored precipitate, it is advisable to treat the filtrate with more Br and $NH_4OH$ and refilter if a precipitate forms.

2. The residue containing the Si, Pb, Mn, Fe and Al is washed with a 2% solution of $NH_4Cl$, six times. The filtrate contains all of the calcium (and magnesium) free from substances commonly interfering in its determination.

Note. If $H_2S$ has been used in the removal of elements in the previous group the filtrate is boiled to remove the gas, the solution having been made acid with HCl.

3. *Precipitation.* — The filtrate containing the calcium is made ammoniacal and then an excess of ammonium oxalate is added (theoretically 1 cc. of 4% $(NH_4)_2C_2O_4.H_2O$ precipitates 0.0158 g. CaO, in practice at least twice this amount is recommended) and the solution heated to boiling and boiled 5 to 10 minutes.

4. The precipitate is allowed to settle (preferably in a warm place) and the clear supernatant solution is tested for calcium by addition

of more oxalate reagent to be sure that a sufficient amount has been added.

5. The clear solution is decanted through a filter and the oxalate in the beaker washed twice by decantation. If the sample contains much magnesium it is advisable to dissolve the precipitate by adding water and just sufficient HCl to effect solution. The acid solution is poured through the filter into a clean beaker. The filter washed three times with water and once with dilute $NH_4OH$ (2% solution).

6. The filtrate is made ammoniacal (the calcium oxalate reprecipitates) and 5 to 10 cc. ammonium oxalate reagent added. The mixture is again heated to boiling, allowed to settle and the oxalate filtered off and washed at least six times with hot water.

7. The pure calcium oxalate is ignited in a weighed crucible (drying being unnecessary) cautiously over a low flame until the paper is consumed and finally over a blast lamp until the weight is constant.

(An electric furnace may be used to advantage for this ignition.)

8. The resulting residue is weighed directly as CaO.

Factors. $CaO \times 0.7146 = Ca$, or $\times 1.7847 = CaCO_3$ or $\times 2.428 = CaSO_4$.

Notes. Calcium sulphate, gypsum, will not yield readily to the acid treatment for decomposition; a fusion with sodium carbonate is necessary. If platinum crucibles are not available nickel or iron may be used. In this case the fused mass (spread over the sides of the crucible) is best dissolved by adding dilute HCl inside the vessel, placed within a beaker, rather than dipping the entire crucible in dilute acid. This will minimize the action of the acid on the crucible. The beaker should be covered to prevent loss by effervescence.

Since CaO absorbs moisture and $CO_2$ it should be weighed as soon as possible after ignition.

Calcium oxalate dried at 100° C. contains one molecule of water. At 200° C. the water is eliminated. At 500° C. the oxalate begins to decompose with formation of $CaCO_3$. At bright red heat the carbonate breaks down to $CO_2$ and CaO.

**Separation of Calcium from Barium and from Strontium.** — The alkaline earths are converted to nitrates, all moisture expelled by heat, and calcium nitrate extracted from the insoluble nitrates of barium and strontium by a mixture of anhydrous ether and absolute alcohol, in equal parts, or by boiling the dry nitrates in amyl alcohol (*b.p.*, 137.8°C.). Details of the procedure are given under Separations of the Alkaline Earths in the chapter on Barium.

If preferred the oxalate may be precipitated from a solution containing acetate by adding 10 cc. of acetic acid to the neutral solution, followed by oxalic acid and the ammonia until alkaline.

## VOLUMETRIC DETERMINATION OF CALCIUM

### TITRATION OF THE OXALATE WITH PERMANGANATE

This procedure may be applied successfully in a great variety of instances on account of the readiness with which calcium oxalate may be separated. In the presence of iron, alumina, manganese, magnesia, etc., it is advisable to make a reprecipitation of calcium oxalate to free it from adhering contaminations.

The following reaction takes place when potassium permanganate is added to calcium oxalate in acid solution:

$$5CaC_2O_4 + 2KMnO_4 + 8H_2SO_4 = 5CaSO_4 + K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

**Procedure.** — Calcium oxalate, obtained pure, by precipitation and washing according to directions given under the gravimetric determination of calcium, is washed into a flask through a perforation made in the filter paper, the filter is treated with a little warm, dilute sulphuric acid [1] and the adhering oxalate dissolved and washed into the flask. About 25 cc. of dilute sulphuric acid, 1:1 is added and the solution diluted to 250 to 300 cc.

When the precipitate has dissolved, the solution warmed to 60 or 70° C. is titrated with standard potassium permanganate, added cautiously from a burette with constant agitation, until a faint permanent pink color is obtained.

One cc. N/10 $KMnO_4$ = 0.0020 gram Ca,[2] or $\times$ 0.0028 = CaO.

Factors. Ca $\times$ 1.3993 = CaO or $\times$ 2.4974 = $CaCO_3$ or $\times$ 3.3975 = $CaSO_4$ or $\times$ 2.581 = $Ca_3(PO_4)_2$.

#### Phosphate Rocks, Calcium Phosphate, etc.

**Determination of Lime in Presence of Phosphates, Iron, and Alumina.** — Should phosphoric acid be present in the solution, calcium will be precipitated as a phosphate upon making the solution neutral or slightly alkaline with ammonia, and will remain with iron and alumina precipitates.

**Precipitation of Calcium Oxalate in Presence of Iron and Alumina.** — The solution containing the phosphates freed from silica is oxidized by boiling with nitric acid as usual. Ammonia water is added to the cooled solution until a slight precipitate forms, and then citric acid is added in sufficient quantity to just dissolve the precipitate. If this does not readily occur, additional ammonia is added, followed by citric acid until the solution clears, then about 15 cc. of citric acid in excess. The solution is diluted to 200 cc. and heated to boiling. Calcium oxalate is now precipitated by addition of ammonium oxalate. Iron and alumina remain in solution.

**Citric acid,** 70 grams of the acid, $H_3C_6H_5O_7.H_2O$, in a liter of water.

**Wagner's Solution.** — In place of citric acid, the following solution may be used. Twenty-five grams of citric acid and 1 gram of salicylic acid are dissolved in water and made to 1000 cc. Twenty-five to 50 cc. of this reagent is effective in preventing precipitation of iron and alumina.

[1] HCl in moderate quantity may be used in place of sulphuric acid without danger of liberating free chlorine as is the case in presence of iron. — Fleischer.

[2] From the reaction $2KMnO_4$, equivalent to 5O or 10H, reacts with $5CaC_2O_4$ and 5Ca = (5×40) ÷ 10 = 20. A normal solution of calcium = 20 grams Ca per liter. One cc. N/10 solution = 0.002 gram Ca.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Rapid Method for Chemical Analysis of Portland Cement [1]

Before submitting the cement to a chemical analysis it should be passed through a No. 100 test sieve to free it from pieces of clinker too large to be quickly attacked by the acid.

Weigh 0.5 gram of cement into a wide platinum or porcelain dish. The former is the more expensive of the two, but it is a better conductor of heat and there is no danger of contaminating the solution with silica, etc., from the dish, if the evaporation is conducted in platinum. The silica can also be entirely removed from a platinum dish. Now stir up the sample of cement in the dish with 10 cc. of cold water until all lumps are broken up, and add immediately 10 cc. of cold dilute hydrochloric acid (1 : 1). Place the dish on a water bath and evaporate to dryness, stirring occasionally. The water bath will evaporate as fast as anything else and there is no danger of silica spattering, which it is apt to do, unless the operation is very carefully watched, when a hot plate is used. As soon as the contents of the dish are dry, cool, add 10 cc. of dilute hydrochloric acid and 30 cc. of water, digest five or ten minutes on the hot plate, filter and wash ten times with hot water. Evaporate the filtrate to dryness. Cool, add 10 cc. of dilute hydrochloric acid and 50 cc. of water to the contents of the dish, cover with a watch-glass and digest on the hot plate for five or ten minutes. Filter off the slight residue of silica on a 9-cm. filter, wash well (seven to ten times) with hot water and put in a weighed platinum crucible together with the silica obtained from the first filtration. Ignite over the Bunsen burner until all the filter paper is consumed and then ignite strongly over a blast lamp for ten minutes. Cool in a desiccator and weigh as $SiO_2$; multiply the weight by 200 for per cent of silica, $SiO_2$.

Heat the filtrate to boiling and add a faint but distinct excess of ammonia. This can be most conveniently done by means of a bottle, fitted with a siphon tube, the end of which terminates in a jet, connected to it by a short piece of rubber tubing, which is closed by a pinch cock. The bottle stands on a shelf over the reagent table, and the siphon extends to within six inches of the surface of the table. The beaker is placed under the jet, and the ammonia can be very carefully and conveniently added by pressing the pinchcock. After adding the ammonia replace the beaker on the hot plate and boil for five minutes. Remove from the hot plate and allow the precipitate to settle. Filter onto an 11 cm. filter paper and wash once with hot water to collect the precipitate in the cone of the filter. Invert the funnel over the beaker in which the precipitation

[1] Method used in the laboratories of most cement companies and for routine work.

was made and wash practically all of the precipitate into this, allowing the filter to remain in the funnel. Dissolve the precipitate in 20 cc. of 10% nitric acid (1:10) and dilute the solution to 100 cc. Heat to boiling and reprecipitate with ammonia as before. Boil for five minutes, allow the precipitate to settle and filter through the same filter paper as used for the first precipitation. Wash once with hot water. Ignite carefully in a weighed crucible over a Bunsen burner and finally blast for five minutes. Cool and weigh as combined oxides of iron and alumina, $Fe_2O_3 + Al_2O_3$. This precipitate also contains manganese dioxide, phosphoric and titanic acids, all of which are present in small quantities in the cement. Determine the iron oxide as directed further on, and deduct from the combined weights for the alumina, $Al_2O_3$ (phosphoric acid, titanic acid, etc.).

Make the filtrate from the iron and alumina alkaline with ammonia; boil and add 20 cc. of boiling saturated ammonium oxalate solution (or better, 3 grams of solid ammonium oxalate dissolved in 25–50 cc. of boiling water just prior to use). Stir well, allow fifteen minutes to settle, filter on an 11 cm. filter, and wash ten times with hot water, using as little as possible (about 100–125 cc.) to do the work well. Proceed as in A or B.

A. Gravimetric. Place the precipitate in a weighed platinum crucible, ignite, and weigh, after ignition over a blast-lamp to constant weight, as calcium oxide, CaO. Report as such.

B. Volumetric. Transfer the paper and precipitate to the beaker in which the latter was formed, and opening, spread it out against the upper side of the beaker. Wash the precipitate off the paper with a jet of hot water, fold the paper over, add 50 cc. of dilute (10%) sulphuric acid (1:10) to the contents of the beaker, dilute to 150 cc. and heat until the liquid is between 60 and 90° C. Titrate with permanganate solution until the pink color is produced. All this time the paper should be sticking to the walls of the beaker. Now drop this into the solution and stir. The pink color of the latter will be discharged. Finish the titration very carefully by adding permanganate, a drop at a time, and calculate the lime.

If the filtrate from the lime measures over 250 cc., acidify and evaporate until this bulk is reached. This can be rapidly done by using a large (8 in.) porcelain dish in the following manner: Place a piece of wire gauze on a tripod and in the center of this a round piece of thin asbestos paper about the size of a silver dollar. Now place the dish on this and a Bunsen burner turned fairly low under the asbestos dish. The contents of the dish can then be made to evaporate rapidly, without boiling, by regulating the flame. When the solution measures 250 cc., transfer to a beaker. If necessary, cool and, when perfectly cold, add 15 cc. of a 10% solution of sodium phosphate and 25 cc. of strong ammonia. Stir thoroughly and set aside in a cool place for at least six hours. Filter, wash with a mixture of water 800 cc., ammonia (0.96 sp.gr.) 200 cc., and am-

monium nitrate 100 grams; place in a weighed platinum or porcelain crucible and ignite over a low flame until all carbon is burned off. (Do not use the blast lamp.) Cool in a desiccator and weigh as magnesium pyrophosphate, which weight multiplied by 72.38 gives the percentage of magnesia, MgO.

Weigh 1 gram of finely ground cement into a small beaker and add 15 cc. of dilute hydrochloric acid, heat from ten to fifteen minutes and add a little water. Heat to boiling and filter [1] through a small filter, washing the residue well with water and catching the filtrate and washings in a small beaker. Add to the solution 5 cc. of dilute hydrochloric acid and bring to a boil. Add carefully, drop by drop, stannous chloride solution (25 grams in 100 cc. of dilute 1 : 3 hydrochloric acid) until the last drop makes the solution colorless. Add 3 drops in excess. Remove from the burner and cool the liquid by setting in a vessel of cold water. When nearly cold, add 15 cc. of saturated mercuric chloride solution and stir the liquid with a glass rod. Allow the mixture to stand for a few minutes, during which time a slight white precipitate should form. Run in standard bichromate solution carefully from a burette until a drop of iron solution tested with a drop of 1% solution of potassium ferricyanide no longer shows a blue, but instead a yellow color. Multiply the number of cc. of bichromate used by the ferric oxide equivalent per cc. of the bichromate and divide the product by the weight of the sample. The result multiplied by 100 gives the per cent of the ferric oxide in the cement. The most convenient strength for the standard bichromate solution is 3.074 grams of the salt to the liter. One cc. of this solution is equivalent to 0.005 gram ferric oxide. It should be standardized against iron wire or ferrous ammonium sulphate.

Weigh 1 gram of the sample into a small dry beaker and stir it up with 10 cc. of cold water until all lumps are broken up and the lighter particles are in suspension. Add 7.5 cc. of dilute (1 : 1) hydrochloric acid and heat until solution is complete. Filter through a small paper and wash the residue thoroughly. Dilute the filtrate to 250 cc., heat to boiling, and add 10 cc. of boiling 10% barium chloride solution. Stir well and allow to stand overnight. Filter, ignite, and weigh as $BaSO_4$, which, multiplied by 34.29, gives the percentage of $SO_3$.

Place one-half gram of the cement in a clean platinum crucible which has been previously ignited to redness and cooled in a desiccator. Cover with the lid and weigh. Ignite for fifteen minutes over a good blast lamp. Rinse off the crucible lid with hot water to remove volatile salts condensed on the latter. Ignite the lid to redness and cool the crucible and lid in a desiccator. Weigh and the loss in weight multiplied by 200 is "loss on ignition."

[1] May be omitted if the cement practically all dissolves. Most cements do.

### Other Methods. Gravimetric

Calcium may be converted to carbonate, sulphate or fluoride and so weighed. The oxide above obtained may be converted to sulphate by moistening with a few drops of water and then adding a slight excess of sulphuric acid (1:4, dilute). The excess sulphuric acid is driven off by heating over a low flame to $SO_3$ fumes and then more strongly at dull red heat until the excess acid has been expelled. A ring burner reduces the risk of spurting. Addition of a drop or so of ammonia to the cooled residue and reheating assists expulsion of the acid. The residue is weighed as $CaSO_4$.

$CaSO_4 \times 0.2943 = Ca$ or $\times 0.4119 = CaO$ or $\times 0.7352 = CaCO_3$.

## CARBON

**C, at.wt. 12.0; sp.gr. amorp. 1.75–2.10; cryst.; graphite, 2.25; diamond 3.47–3.5585; m.p. sublimes at 3500° C.; oxides, CO and $CO_2$**

### OCCURRENCE

The element occurs free in nature in the crystalline forms, diamond and graphite, and in the amorphous form, charcoal, coke, etc. It occurs in iron, steel, and in certain alloys. Its estimation in these metals is generally required. Carbon is determined in the analysis of organic compounds in which it is invariably combined and may also be present as free carbon (asphaltum).

Combined as a carbonate it occurs in a large number of substances, among which are found calcite, marble, limestone, dolomite, magnesite, strontianite, witherite, spatic iron ore. It occurs as the dioxide in the air, in water ($H_2O.CO_2$) and in flue gas. Carbon dioxide is the active constituent of baking powders ($NaHCO_3$).

**Minerals.** — *Graphite*, C, is a soft, greasy to the touch, black to dark gray opaque mineral with metallic lustre; in impure form it appears slaty or earthy. It occurs as flakes or flexible scales to compact masses, rarely as six sided plates; streak dark-gray; hardness 1–2. Graphite differs from molybdenite in being darker in color, and in the flame it burns to $CO_2$ gas, the latter gives off $SO_2$; graphite is insoluble in acids, molybdenite dissolves in strong nitric and sulphuric acids.

*Diamond*, C, transparent, isometric crystals, with adamantine lustre; usually colorless or slightly tinted, bluish, yellow, brown or green; lustre brilliant when polished; perfect cleavage, parallel to octahedron; specific gravity 3.145–3.518; hardness 10, exceeding that of any other known substance.

Varieties — ordinary diamond rounded crystals with distinct cleavage; Bort, any lower grade diamond not deemed worthy to be cut; Carbonado, a black massive or granular material from Brazil.

Other minerals of carbon — Petroleum, Asphalt, Mineral Coal, Ambrite, Copalite, Ozocerite, etc.[1]

[1] The study of methods of determining carbon should be taken up by the more advanced student. It is advisable to start with the combustion method given on page 182.

## DETECTION

**Element.** — Carbon is recognized by its appearance and by its inertness towards general reagents. It is seen in the charring of organic matter when heated or when acted upon by hot concentrated sulphuric acid.

Upon combustion with oxygen or by oxidation with chromic and sulphuric acids, carbon dioxide is formed. The gas passed into lime water forms a white precipitate, $CaCO_3$.

**Carbon Dioxide. Carbonates. $CO_2$ in Gas.** — A white precipitate with lime water, baryta water, ammoniacal solutions of calcium or barium chlorides, or lead acetate (basic); carbonates of the metals are formed.

**Carbonates.** — Action of mineral acids causes effervescencé, $CO_2$ being evolved. The gas is odorless (distinction from $SO_2$, $H_2S$, and $N_2O_3$) and is colorless (distinction from $N_2O_3$). The gas absorbed in the reagents above mentioned produces a white precipitate. The test is best made by placing the powdered material in a large test-tube with a stopper carrying a funnel and delivery tube as shown in the illustration, Fig. 50. For small amounts of combined $CO_2$, warming of the test-tube may be necessary. Sulphuric or phosphoric acid should be used to liberate the gas, which is conducted into the reagent used for the test.

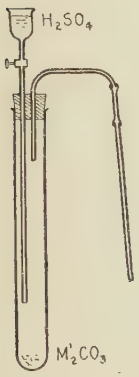


FIG. 50. — Test for Carbonate.

**Distinction between Carbonates and Bicarbonates.** — The solution of the former is alkaline to phenolphthalein indicator (pink). Bicarbonate solutions remain colorless with this indicator. Normal carbonates precipitate magnesium carbonate when added to magnesium sulphate solution; bicarbonates cause no precipitation.

**Free Carbonic Acid in Water in Presence of Bicarbonates.** — 0.5 cc. of rosolic acid (1 part acid in 500 parts of 80% alcohol), produces a red color with bicarbonates in absence of free $CO_2$, and a colorless or faintly yellow solution when free $CO_2$ is present.

**Carbon Monoxide.** — The gas burns with a pale blue flame and is not absorbed by potassium hydroxide or lime water (distinction from $CO_2$). It is oxidized to $CO_2$ and so detected. With hot, concentrated potassium hydroxide, potassium formate is produced.

The gas is detected in the blood by means of the absorption spectrum.

## GRAVIMETRIC METHODS FOR DETERMINATION OF CARBON

### Preparation of the Sample

**Iron, Steel, and Alloys.** — Drillings taken from different sections of the representative bar should be free from grease and dust. These are best kept in glass-stoppered bottles. Where a large number of daily samples are determined, it is found more convenient to use small manila envelopes, upon which the record of the analysis may be placed. Should it be impossible to obtain drillings free from grease, this impurity may be removed by heating the sample in an atmosphere of nitrogen, or by repeated extraction with ether.

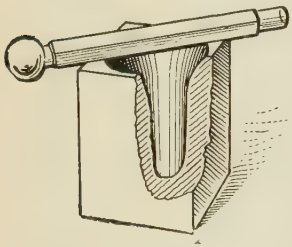


Fig. 51. — Chilled-Steel Mortar.

Coarse chips, cast-iron drillings, etc., should be broken down in a chilled-steel mortar. Fig. 51.

Carbon may now be separated in a definite weight of the sample as directed below, or it may be determined by direct combustion or by oxidation with chromic acid according to a procedure given later.

**Organic Matter.** — It is advisable to fuse this in a nickel or iron crucible with sodium peroxide. The carbonate thus formed may be determined as usual. The organic substance may be oxidized directly in the combustion furnace.

**Carbonates. Limestone, Dolomite, Cement, Alkali Carbonates and Bicarbonates.** — The powdered material is decomposed by addition of an acid as directed in the methods given later.

### Separation of Carbon from Other Substances

The element is generally determined as carbon dioxide, in which form it is liberated from most of the combinations in which it occurs, free from other substances by ignition in a current of oxygen, or by oxidation with chromic acid as directed later.

**Separation of Carbon in Iron and Steel. Cupric Potassium Chloride Method.** — 0.5 to 2 grams of the drillings are treated with 100 to 200 cc. of cupric potassium chloride solution and 10 cc. of hydrochloric acid (1.19). This mixture dissolves the iron according to the reaction

$Fe + CuCl_2 = FeCl_2 + Cu$ and $Cu + CuCl_2 = Cu_2Cl_2 +$ carbon as a residue.

The determination of carbon by combustion with oxygen is made in two general classes of substances: *A*. Steel, iron and in certain

alloys. *B.* Organic compounds. Carbon in steel and alloys is considered in two forms: carbide or combined carbon, and graphitic carbon. In organic substances carbon occurs principally combined with hydrogen, oxygen, and nitrogen. For the present we will consider procedures for the determination of carbon in steel and alloys.

The most accurate procedure for determination of carbon in steel, alloys, and in other materials containing the substance combined or free is by combustion with oxygen in a furnace heated by gas or electricity; the carbon dioxide formed being absorbed in caustic, and weighed.

**Apparatus. Combustion Furnace.** — Although the gas furnace has been used more commonly on account of gas being more available than electricity, the extension of generating electric plants makes it possible to use electric furnaces, and these are gradually displacing those heated by gas, as they are more compact, easily manipulated and comparatively simple in structure.

A simple electric furnace may be made by wrapping a silica tube with a thin covering of asbestos paper, which has been moistened with

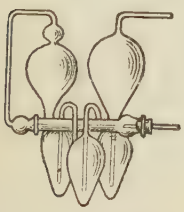


FIG. 52. — Geissler Bulb.

FIG. 53. — Liebig Bulb.

FIG. 54. — Gerhardt Bulb.

water. On drying the paper will cling to the tube. A spiral coil of nichrome wire (Driver and Harris) is wound around this core. On a 2-foot length of tube two 45-foot lengths of No. 18 wire, connected in parallel, will heat the tube to bright redness, attaching the terminals to an ordinary light socket. The coils should be covered with $\frac{1}{4}$-in. coating of alundum cement. For appearance' sake as well as for protection, the tube is placed in a large cylinder of sheet iron, packed around with asbestos, and is held in position by circular asbestos boards placed at the ends of the large cylinder. The cylinder is mounted on a stand.

**Absorption Apparatus.** — A large number of forms are for sale. The Geissler and Liebig bulbs have been popular (Figs. 52 and 53), but are now being displaced by forms that have less surface exposed, that are more easily cleaned and less fragile, such as Gerhardt's, Vanier's and Fleming's apparatus (Figs. 54, 55 and 57).

## CABBON DETERMINATION IN STEEL

**Procedure for Determining Carbon by Combustion.** — By this method absolutely accurate results can be reported to the open hearth ten minutes after the drillings are received.

In principle this method is not new; in manipulation it is new. Heretofore chemists have been laboring under the impression that the flow of gas during a combustion must not exceed a certain snail-like pace. This false impression has been injected into the minds of chemists by a few who were supposed to have investigated the matter. The truth is that the faster oxygen is fed to burning steel the more complete the combustion will be. The rate of current is limited by the efficiency of the apparatus used to absorb the evolved carbon dioxide.

Fig. 55. — Vanier Bottle

**The Apparatus Described.** — The combustion train is shown complete in Fig. 56. The oxygen is delivered to the train through a regulating and reducing valve such as is used for welding. The [regulating valve is not essential, yet any chemist who uses one will appreciate its convenience, especially in this method. Its convenience will be explained later. *K* is a mercury pressure gauge. It serves as a guide during the combustion and is an essential piece of apparatus. The graduated column is 6 ins. high and is divided into eighths. *P* is a washing bottle containing caustic potash solution. Filled to the mark indicated with 50% solution it will serve for at least 1000 combustions. It is used solely to indicate the flow of gas, not to purify it. If the chemist desires he may omit this from the train. *T* is a calcium chloride jar. It is filled to the mark indicated with finely divided calcium chloride, about pea size, retaining all the dust. A layer of asbestos is formed over the chloride and the remaining space filled with soda lime. The glass tubing leading from the jar is loosely packed for a distance of several inches with asbestos. This prevents any soda lime dust being carried into the combustion tube. *G* is a mercury valve like that used in Johnson's train. It is used solely to maintain an atmosphere of pure oxygen in the purifying train, a condition essential to accurate results. It is not used to prevent carbon dioxide backing into the purifying train, of which there is not the remotest possibility.

Note. To increase accuracy conduct the weighings with two absorption bulbs, of the same kind, one used to absorb the carbon dioxide, the other as

a tare weight. During the run the tare is placed side by side with the one in the train. With the run complete the tare is placed in the right pan of the balance and the absorption bulb with the $CO_2$ in the left. It is not advisable to wipe off the bulbs as the condensation is the same on both.

The combustion tube is the ordinary fused silica tube glazed on the inside only. The tube is 30 ins. long with inside diameter of from 7 to 1 in. One tube of 30 ins. will serve twice as long as one of 24 ins. It is loosely packed with asbestos for a distance of 6 ins. at the exit end, and 3 ins. is allowed to project from the furnace. For about the first 100 combustions, the combustion boat is pushed close against the asbestos. The portion of the tube immediately above this will become coated with iron oxide. The asbestos is then moved up so that it covers this portion of the tube and a fresh area exposed to the spraying oxide. In this manner one tube can be made to serve 600 combustions or even more.

**The Furnace and Combustion Tube.**— The furnace used is one of the ordinary resistance type. It is constantly maintained at a temperature of 1000° C. This temperature is verified daily by the use of a pyrometer. Many claim to be expert at judging temperatures, but none are expert enough to be without a pyrometer. The two-way stop following the combustion tube will be found very convenient when it is not desirable to pass the current through the jars *Z* and *O*.

*Z* is filled with 20-mesh zinc. Once filled it will serve for several thousand combustions. As a matter of fact it is included in this train as a filter. If nickel boats and aluminum are used the chemist may omit this zinc jar from the train, for with all ordinary grades of steel it serves no purpose.

*O* is the phosphoric anhydride jar. A little asbestos is placed in the lower part just above the lower stopper. The remaining space in the jar is completely

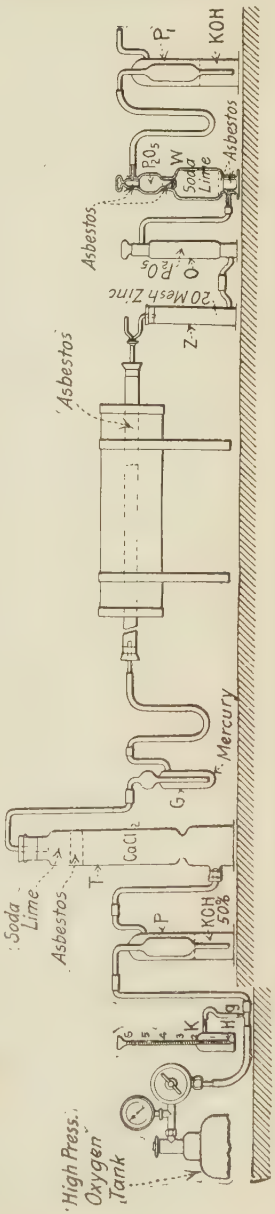



FIG. 56. — Fleming's Apparatus for Determination of Carbon by Combustion.

filled with phosphoric anhydride. The upper stopper is packed tightly enough to prevent any powder being swept into the weighing apparatus. As the anhydride liquefies it passes down into the lower stopper, where it can be removed conveniently without disturbing the anhydride above it. Likewise the anhydride can be replenished by removing only the upper stopper. The jar need not be washed oftener than once in 500 combustions. When filled with anhydride, fresh reagent need not be added for at least 150 combustions. After each combustion the jar should be given a few sharp taps with the hand to prevent canals being formed.

**Details of the Absorption Apparatus.** — The absorption apparatus, shown in detail in Fig. 57, has been modified slightly at the suggestion of Henry G. Martin, of the Railway Steel Spring Company, Chicago Heights, Ill. This apparatus is no more efficient than the old style, but it is much more convenient and less troublesome. In the old-style tube the anhydride would liquefy after several days and require replenishing. To overcome this, Mr. Martin suggested using separate chambers for the anhydride and soda lime, so that communication could be broken when the tube was standing idle. The tube shown in Fig. 57 will serve for at least 70 combustions when operating on 1.5 grams of sample containing 1.03% carbon.

Fig. 57.—Fleming Absorption Apparatus.

The anhydride in the upper chamber serves for at least 300 combustions. Soda lime, placed in the lower tube in alternate layers ($\frac{1}{8}$ in.) of the different meshes, has proven a very convenient and desirable reagent. The 12-mesh soda lime for nitrogen can also be used with excellent results. If this is employed, part of it should be ground to about 60-mesh and alternate layers of fine and coarse used.

It is exceedingly important that the tube be loaded with alternate layers of coarse and fine reagent, for, if the 12-mesh reagent is transferred directly from the bottle to the absorption tube, the latter will fail to be effective for more than 30 combustions and in some cases less. The reason for this is evident. The lower stopper is packed loosely with asbestos, also the lower portion of the soda lime chamber just above the stopper. Beginning with a layer of 12-mesh soda lime, the entire chamber is filled with alternate layers of fine and coarse reagent. The small diameter of the anhydride chamber is packed with asbestos and the remaining space filled with phosphoric anhydride. Finally, the upper stopper is packed with asbestos. The anhydride chamber, filled as indicated, will not require refilling for at least 300 combustions. It is not necessary to turn the chamber to break communication while the tubes are idle, for the packing of the small diameter with asbestos prevents the absorption of moisture from the

soda lime. The tubes must be used in pairs, so that one serves as a tare in weighing the other. A pair of tubes assures the operator of at least 140 combustions. A glass or rubber tubing about 12 ins. long serves as a guard for the absorption tube. It connects the bottle, $P_1$, which is used to indicate flow of gas.

The use of clay boats has been abandoned in favor of nickel boats filled with alundum. These are greatly superior to clay boats in every conceivable way. The alundum is labeled as being free from carbon, but this is not true. In fact, some of it contains cosiderable carbon. It should always be burned in oxygen at 1000° C. before using. The boats are formed out of 22-gauge pure sheet nickel. One boat will serve for about 100 to 150 combustions, some more, some less.

**Details of the Analysis.** — The furnace being at 1000° C., the two freshly prepared absorption tubes are placed in the train and oxygen run through at the rate of 300 cc. per minute for fifteen minutes. This insures the displacement of all air from the purifying train as well as the absorption tubes. Remove one absorption tube from the train and turn on the oxygen until the mercury stands at about 2 ins. The rate of current is then measured by inverting a graduated cylinder filled with water. Several trials will establish a rate of about 325 cc. per minute. Note the reading of the column of mercury at this rate and subsequently, when using the same absorption tube, maintain this same pressure in the train and the rate of flow will be 325 cc., the rate during all combustions. Shut off the oxygen and, when it comes to a slow bubbling through $P_1$, close the upper stopper of the absorption tube. Disconnect it from the train, but do not close the lower stopper for about five seconds after disconnection. Weigh against its mate as a tare. It is now ready for the first combustion.

Weigh 1.5 grams of drillings, preferably thin, curly drillings from a twist drill, and spread out in the nickel boat which is half filled with alundum. Place the absorption tube in the train and place its mate beside it. With the oxygen flowing about 100 cc. per minute, the drillings are pushed into the combustion tube. The current is immediately run up to the desired pressure, which gives 325 cc. per minute. The regulator will do the rest. It will feed the oxygen automatically to the burning steel. As a rule the drillings are entirely burned one and one-half minutes after insertion. Continue the flow of oxygen for three and one-half minutes more (five minutes, total time) and disconnect as before the absorption tube. Weigh immediately. The result will be accurate and reliable. Whether determining carbon in a standard steel, where the greatest accuracy is required, or in a bath test, the time required is always five minutes.

The weight of the boat, plus refractory lining, should be kept as low as possible, so as not to introduce too much cold material into the combustion tube. The boats used are preferably $\frac{1}{2}$ in. wide, 1 in. deep and 3 ins. long. Sheet nickel varies in percentage of carbon. As

a rule, a nickel boat must be ignited in oxygen at 1000° C. for one to two hours.

There seems to be a difference of opinion concerning the physical condition of the steel after burning, some chemists believing that inaccurate results are obtained if the drillings have fused during combustion. Others maintain that complete fusion of the drillings is essential to accurate result. If drillings which happen to be a little thick are used, low results are obtained unless these are *perfectly fused.*

### Stetser and Norton Combustion Train for Carbon Determinations

By the use of this apparatus the usual procedure is to allow three or four minutes for combustion. Results are often reported in six minutes after the sample enters the laboratory: this includes time for drilling, weighing sample, running test, weighing bulb and reporting result.

The oxygen is delivered from a high pressure cylinder through the gas pressure regulator, and the authors also recommend that bottles as shown in the illustration be used to measure the amount of gas consumed and to supply rapidly the extra quantity of oxygen required during the burning of the drillings, in addition to equalizing the pressure.

**Method of Operation.** — The train is set up free from leaks, and the stopcocks are opened with the exception of the one on the Sulphuric Acid Bulb K. This is opened sufficient to allow gas to flow at the rate of 200 to 250 cc. per minute when the Absorption Bulb is attached.

The stopcock C is then closed, the remaining stopcocks being left as adjusted. The train is now ready for operation. Bottle B is filled with water. The gas regulator is opened, allowing oxygen to displace the water in bottle B, which water is driven into bottle *A*. When bottle A is filled, the regulator is closed and the train is ready for the combustion. The exit end of the combustion tube, the usual glazed silica tube being recommended, is packed with some asbestos burned in a current of oxygen prior to using.

A sample of one-half factor weight properly prepared and weighed is placed in the alundum boat, RR Alundum protection being used, and then inserted in the furnace. The stopcock C is opened, and if the furnace is at 1000° C. or over, and the sample of drillings fine and uncovered, it should begin to burn in 20 seconds. The burning should take 40 to 60 seconds additional, consuming 500 cc. of oxygen. An additional 500 cc. of oxygen is turned on to wash out all $CO_2$, and the bulb is then ready to be weighed.

If the sample is covered by a lid or RR Alundum, or if the drillings are coarse, or the furnace is below 1000° C., the combustion may be delayed as much as two minutes. The actual burning will, as before,

take from 40 to 60 seconds. In any event, 500 cc. of gas must be passed through the apparatus after the steel has ceased burning. The point at which the burning of the sample begins may be determined by the increased rate at which gas passes through the liquid in

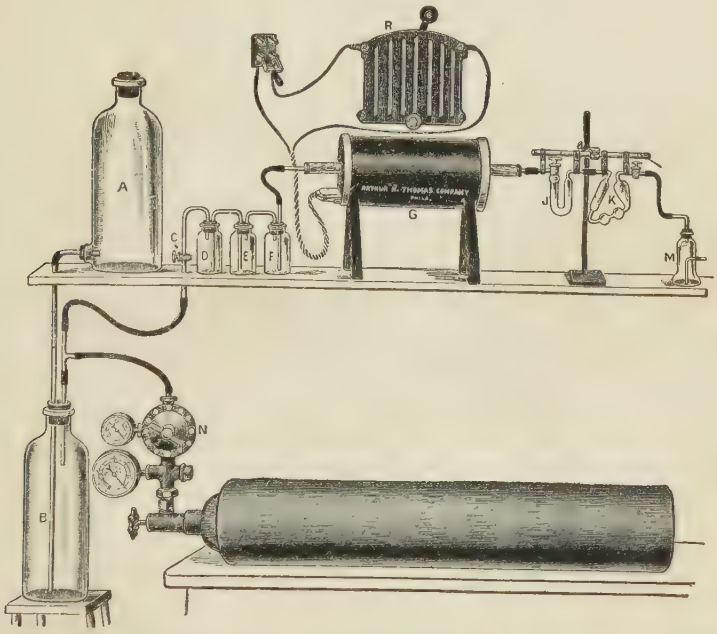



FIG. 58. — Stetser and Norton Combustion Train for Carbon Determinations.

**A** **Aspirator Bottle,** 8 liters capacity, graduation interval 250 ml., with one hole rubber stopper.
**B** **Bottle,** narrow mouth, of green glass, 2 gallons capacity, with two hole rubber stopper.
**Glass Tubing,** 6 mm. outside diameter, for connections.
**Glass T-tube,** 3 mm. bore.
**C** **Glass Stopcock,** 2 mm. bore; used to prevent the gas from flowing through the train when turned on at the regulator.
**D** **Bottle,** wide mouth, 8 oz. capacity, with two hole rubber stopper; to be used empty as a safety.
**E** Ditto; to be filled one third full with concentrated Sulphuric Acid.
**F** Ditto; to be filled with Ascarite.
**Combustion Tube, of Silica,** glazed, 30 inches long by $\frac{3}{8}$ inch diameter.
**G** **Combustion Tube Furnace.**
**R** **Rheostat,** for controlling the temperature.
**J** **Vanier Zinc Drying Tube;** to be filled with 30 mesh Zinc.
**K** **Vanier Sulphuric Acid Bulb;** to be filled with Sulphuric Acid.
**M** **Stetser and Norton Modification of the Midvale Absorption Bulb.**

bottle E, due to the rapid absorption of oxygen by the burning steel. A similar decrease marks the end of the burning period.

**Standardization of the Stetser and Norton Absorption Bulb.** — A freshly filled bulb should be run on the train for an hour and then

weighed. When the bulb has reached a constant weight, the train is checked by running a government standard.

A bulb once filled and standardized will last for several weeks and

FIG. 58a. — Hutchinson-Weirich Combustion Bulb for the Rapid Absorption of $CO_2$ in Carbon Determinations in Iron and Steel.

is sufficient for from three to four hundred determinations. On account of the difference in color between the used and unused portions of the absorbent, it is possible to determine the moment a bulb can be discarded.

## GRAPHITIC CARBON

**In Iron and Steel.** — The sample of 1 gram of pig iron or 10 grams of steel is treated with 15 cc. of nitric acid (sp.gr. 1.2), per gram of sample taken. When all the iron has dissolved, the graphite is allowed to settle and the supernatant liquid decanted onto an ignited asbestos filter, using either a perforated boat, Fig. 59, or a filtering tube. The residue is transferred to the filter, and washed thoroughly with hot water. It is treated with hot caustic solution (sp.gr., 1.1), washed thoroughly again with hot water, then with a little dilute hydrochloric acid, and finally with hot water. The carbon is now burned by one of the procedures given — the oxidation in the combustion furnace being recommended. The $CO_2$ is absorbed in caustic and estimated according to the standard procedure given for carbon.

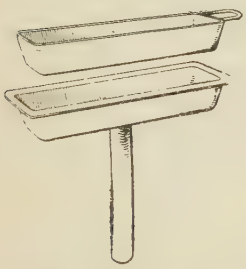


Fig. 59. — Boat and Holder for Carbon Determination.

$$CO_2 \times 0.2727 = \text{graphitic carbon.}$$

The perforated boat, shown in the cut, fits snugly into the receptacle below. Sufficient asbestos is poured into the boat to form a film over the bottom. A seal is made around the boat with additional asbestos, the apparatus having been inserted in a rubber stopper in the neck of a suction flask and suction applied.

The apparatus is recommended by Blair for combustion of graphitic carbon or of total carbon liberated from iron or steel by the cupric potassium chloride method. The boat may be placed directly in the combustion tube and the carbon oxidized as usual.

## COMBINED CARBON

**Indirect Method.** — The excess of carbon remaining when the graphitic carbon is subtracted from total carbon (in iron and steel), is calculated as combined carbon. This "difference method" is generally accepted as being the most accurate for estimation of combined carbon.

Notes. In chromium, tungsten and titanium steels a temperature of 1500° C. is necessary to oxidize the carbon by direct combustion for thirty minutes. (J. R. Cain and H. E. Cleaves, J. Wash. Acad. Sci., **194**, 4, 393–397.)

*Carbon in Soils.* One to 3 grams of 60-mesh sample is treated with a solution of 3.3 grams $CrO_3$ + 10 cc. $H_2O$ and 50 cc. conc. $H_2SO_4$ (1.84). The evolved $CO_2$ is absorbed in standard caustic and titrated with acid, phenolphthalein and methyl orange being used as indicators. (J. Ind. Eng. Chem., 1914, **6**, 843–846.)

## DIRECT COLORIMETRIC METHOD FOR DETERMINATION OF COMBINED CARBON

The procedure is of value to the steel laboratory where a large number of daily determinations of combined carbon are required. By this method over a hundred determinations a day be made by an experienced manipulator. The method depends upon the color produced by combined carbon dissolved in nitric acid, the depth of color increasing with the combined carbon content of the material. Comparison is made with a standard sample of iron or steel, which is of the same kind and in the same physical condition as the material tested. That is to say, a Bessemer steel should be compared with a Bessemer standard, open hearth with open hearth, crucible steel with crucible steel, the standards containing approximately the same amounts of carbon, and as nearly as possible the same chemical composition. The samples should be taken from the original bar which has not been reheated, hammered, or rolled. Copper, cobalt, and chromium will interfere with the test; the other elements have very little effect.

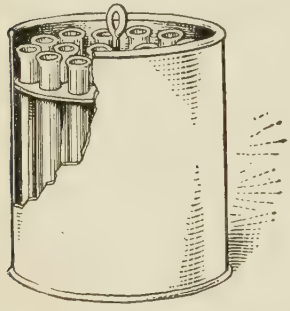


FIG. 60. — Hot Water Rack for Test Tubes.

**Procedure.**— One standard sample of 0.2 gram and the same amount of sample drillings are taken for analysis. The weighings are conveniently made in brass or aluminum pans, boat-shaped to enable the drillings to be dumped into test-tubes. A counterpoise, weighing the same as the boat, is placed on the opposite pan, together with the 0.2 gram weight. A magnetized knife will assist in removing the excess of material. The weighed sample is brushed into a test-tube 6 in. long (150 mm.) 0.6 in. (16 mm.) in diameter. (Each test-tube has a label near the open end to distinguish the sample.) A rack or a 600-cc. beaker may be employed for holding the test-tubes during the weighing. After the batch is ready the tubes are transferred to a perforated rack (Fig. 60) and this then stood in the water bath filled with cold water.

The proper amount of nitric acid (sp.gr. 1.2; e.g., 1 conc. $HNO_3$ : 1 $H_2O$), from a burette, is now added to each test-tube.

3 cc. $HNO_3$ for 0.3% C.
4 cc. $HNO_3$ for 0.3 to 0.5%
5 cc. $HNO_3$ for 0.5 to 0.8% C.
6 cc. $HNO_3$ for 0.8 to 1% C.
7 cc. $HNO_3$ for over 1% C. steel.

The depth of color produced by the acid will give an idea of the amount required. One cc. of acid is added at a time until the depth of color is correct. This requires experience gained from observation

of the color produced by standard samples. The acid is added slowly to the coarse drillings. Insufficient acid gives a darker tinted solution than it properly should be. The nitric acid should be free from chlorine and hydrochloric acid, since these produce a yellow color. (Cl and $FeCl_3$ are yellow.)

A glass bulb or a small funnel is placed in each test-tube and the water in the bath then heated to boiling and boiled until all the carbonaceous matter has dissolved, the tubes being shaken from time to time to prevent formation of a film of oxide. Low-carbon steels require about twenty minutes, whereas steels of over 1% carbon require about forty-five minutes. (Blair.) As soon as the bubbles cease and the brownish flocculent matter disappears, the rack is removed from the bath and placed in a casserole of cold water. (Prolonged heating and strong light each causes fading of the color due to com-

Fig. 61. — Carbon Tubes.

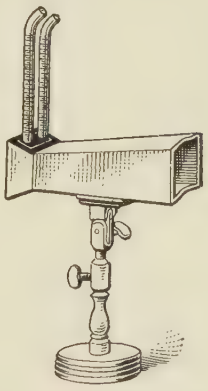


Fig. 62. — Color Comparator or Camera.

bined carbon.) In presence of graphitic carbon, filtration of the solution may be necessary to remove the insoluble suspended graphite.

**Color Comparison.** — This is made in graduated, clear, colorless, cylinders called carbon tubes. The form shown in Fig. 61 was found by the writer[1] to be the most satisfactory type for a steel-works laboratory where rapidity of manipulation was essential. The bend at the upper portion of the tube facilitates mixing of the solution upon dilution with water, the tube being tilted back and forth until the solution is homogeneous, the bend preventing the liquid from spilling. The dilution should be at least twice that of the amount of nitric acid used, as this amount of water is necessary to fade the color due to ferric nitrate.

The standard is poured into the carbon tube and the rinsings from the test-tube added. The solution is diluted to a convenient multiple

[1] W. W. Scott.

in cc. of the carbon content. For example, 0.45% carbon sample may be diluted to 9 cc., then each cc. will represent 0.05% carbon. The sample is placed in a second tube of exactly the same diameter, wall thickness, and form. If the solution of the sample is darker than the standard, water is added little by little, followed by mixing, until the shade matches the standard. If the standard, on the other hand, is darker than the sample, a greater dilution of the standard is necesary, the cc. again representing a multiple of the carbon content. For example dilution of the .45% carbon sample to 15 cc. makes each cc. to represent 0.03 carbon. (It is frequently advisable to take a standard of lower carbon content in place of greater dilution of the standard.)

**Example.** – Suppose in the first case the dilution of the sample was 15 cc. in order to match the standard, then $15 \times 0.05 = 0.75\%$ carbon. Six cc. dilution case $2 = 6 \times 0.03 = 0.18\%$ carbon.

The color comparison can be best made in a " camera," a long box with one end closed by a ground-glass screen, Fig. 62. Parallel to the screen and near it, two holes through the top of the box admit the test-tubes. The inner walls of the camera are blackened to prevent reflection of light. If a camera is not available, the tubes may be held side by side and compared against a sheet of white paper held as background.

## BENEKER'S MODIFICATION OF EGGERTZ'S METHOD FOR DETERMINING CARBON IN STEEL

By this procedure interference of the color due to iron is eliminated. .2 g. of the sample and standard (which does not need to be very similar in carbon content to the sample) are weighed into two test tubes, treated with 7 cc. – 10 cc. of nitric acid of the usual dilution, say 3 parts water to 2 parts acid, and warmed until dissolved and perfectly clear. When cold, $\frac{1}{2}$ cc. of 85% phosphoric acid is added to each tube, transferred to the comparison tubes and read. When this method is used on low carbon steel the bleaching action is very pronounced, because in that case the iron color bleached out represents the major part of the original color. Dilution of standard or sample introduces no error, because of the absence of the interfering iron color.

## DETERMINATION OF CARBON IN GRAPHITE

The procedure for determining carbon in graphite is the same as that described for determination of carbon in difficultly combustible organic substances.

The material is broken down in a steel mortar and powdered in an agate mortar. About 0.2 gram is taken for the determination and mixed with copper oxide to assist the combustion, then placed in the boat and the combustion of the carbon carried on according to the standard method in the combustion tube.

$$CO_2 \times 0.2727 = C.$$

## DETERMINATION OF CARBON DIOXIDE IN CARBONATES

The method is applicable for determination of carbon dioxide in limestone, dolomite, magnesite, strontianite, witherite, spatic iron ore, carbonates of sodium, and potassium, bicarbonates in baking powder, carbon in materials readily oxidized to $CO_2$ chromic sulphuric acid

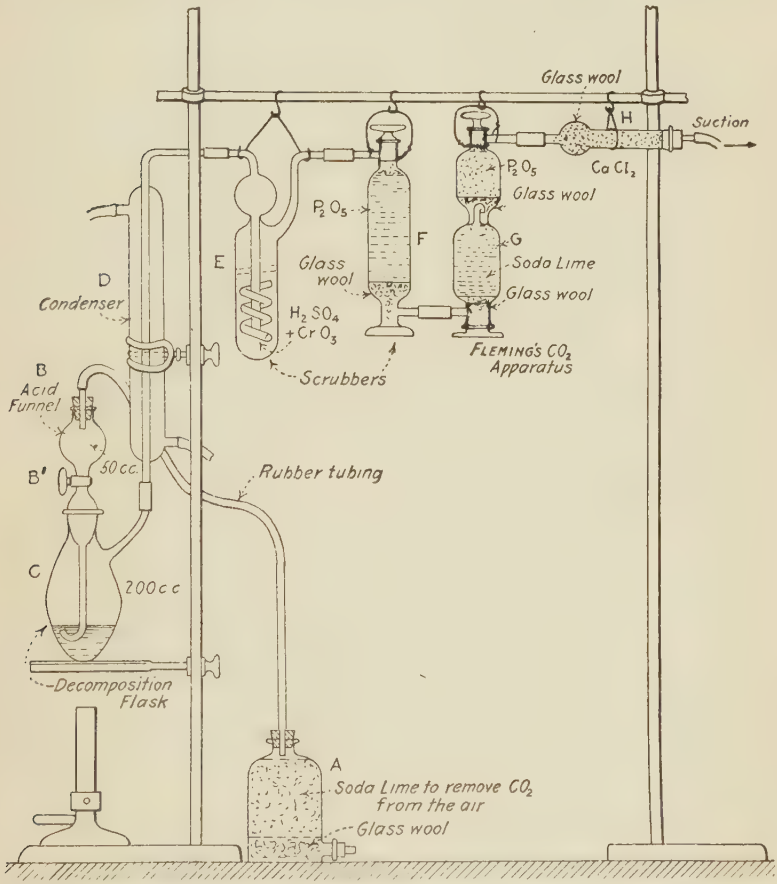



Fig. 63. — Apparatus for Determining Carbon Dioxide.

mixture. The procedure depends upon the evolution of carbon dioxide by a less volatile acid, or the oxidation of carbon. The $CO_2$ is absorbed in caustic and weighed.

**Apparatus.** — The illustration shows the apparatus found suitable for this determination. It is Knorr's apparatus slightly modified. The

absorption bulb or bottle should be one that will effectively absorb carbon dioxide entering at a rapid rate. The Vanier or the Fleming forms is satisfactory for this purpose.

**Procedure.**— A sample weighing 0.5 to 2 grams, according to the carbon dioxide content, is placed in the dry decomposition flask (*C*). The flask is closed by inserting the funnel tube (*B*) fitted with the soda lime tube (*A*), and connected by means of a condenser to the train for removing impurities from carbon dioxide, leading to the absorption bulb, as shown in Fig. 63.

The apparatus is swept out with a current of dry, purified air before attaching the weighed absorption bottle. This is accomplished by applying gentle suction at the end of the purifying train. The absorption apparatus is now attached (Fleming absorption apparatus is shown in the illustration). The tube (*B*) is nearly filled with dilute sulphuric acid (1:3), the stop-cock (*B'*) being closed. The soda lime tube is now inserted into place as shown in the cut. The acid in (*B*) is now allowed to run slowly down on the sample at a rate that evolves gas not too rapidly to be absorbed; 1 to 2 cc. of acid being retained in (*B*) to act as a seal, the stop-cock (*B'*) being then closed.

When the violent action has ceased, the solution in (*C*) is heated to boiling and boiled for about three minutes. Gentle suction is now applied to the absorption end of the apparatus and the stop-cock (*B'*) opened, allowing the remainder of the acid to flow into the flask (*C*) and admitting a current of air, purified by passing through the soda lime in (*A*). The suction should be gentle at first, and then the speed of the flow increased to the full capacity of the absorption bottle. A fairly rapid current is preferred to the old-time procedure of bubbling the gas through the apparatus at a snail-like pace, but discretion should be used in avoiding a too rapid flow.

By gently heating to boiling during the passage of the air, steam assists in expelling any residual $CO_2$ in the flask. When the passage of air is rapid, this boiling should be discontinued.

The increase of weight of the absorption bottle is due to the carbon dioxide of the sample. This procedure gives total $CO_2$.

## DETERMINATION OF CARBON DIOXIDE BY LOSS OF WEIGHT[1]

An approximate estimation of the carbon dioxide in carbonates — baking powders, bicarbonate of soda, limestone, etc., may be obtained by the loss of weight of the material when treated with a known weight of acid.

Various forms of apparatus are used for this determination. The Schroetter and Mohr types are shown, Figs. 64 and 65.

About 0.5 to 1.0 gram of sample is taken and placed in the bottom of the flask, dilute hydrochloric and strong sulphuric acids then placed in the bulbs as indicated in the illustrations. The apparatus is

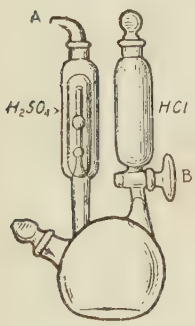



FIG. 64. — Schroetter's Alkalimeter.

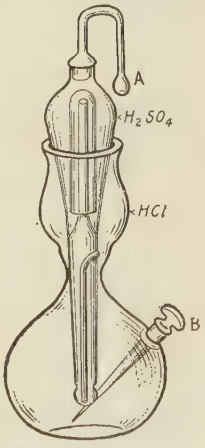



FIG. 65. — Mohr's Alkalimeter.

weighed as it is thus charged. The hydrochloric acid is now allowed to flow down on the carbonate and the stopper closed. The evolved gas passes through the strong sulphuric acid, which absorbs the moisture. After the vigorous action has subsided the apparatus is placed over a low flame and the solution heated to boiling and boiled very gently for about three minutes. No steam or vapor should pass through the sulphuric acid as this would make results worthless, the water lost being calculated as $CO_2$. $CO_2$-free air is aspirated through the solution to expel the last traces of $CO_2$, by applying very gentle suction at *A* and opening *B*, aspirating pure air by connecting *B* to a soda lime tower to remove any $CO_2$. The apparatus is again weighed and the loss of weight taken as the $CO_2$ of the material.

Available $CO_2$ in baking powder may be determined by substituting water in place of hydrochloric acid.

[1] See hydrometer method in Standard Methods of Chemical Analysis, by W. W. Scott.

## DETERMINATION OF $CO_2$ IN CARBONATES — HYDROMETER METHOD OF BARKER

The method depends upon the principle of the hydrometer, following the law that when an object is immersed in a liquid it is buoyed up by a force equal to the weight of the liquid displaced by the object. The carbon dioxide set free from the sample decreases the weight; and the rise of the graduation scale tube above the water records the percentage of carbonates from which the gas was released.

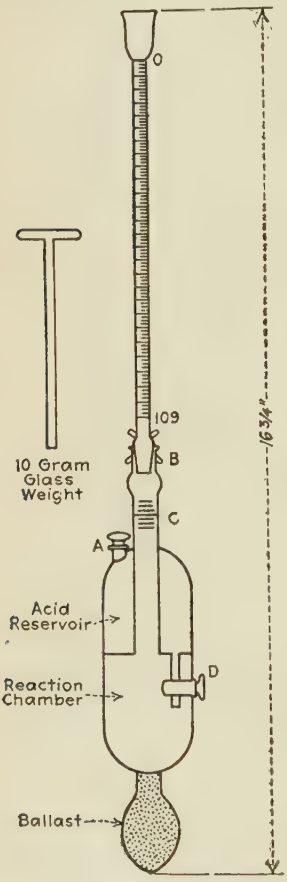



FIG. 66. — Barker's Hydrometer.

**Procedure.** — To analyze a sample for carbonates measure out 40 cc. of hydrochloric acid (sp.gr. 1.15), using a small graduate; pour this into the acid reservoir through the opening *A*. With graduated stem disconnected hang a 10 gram weight at *B*. The hydrometer should then float in a cylinder of water and be immersed to some point at *C*. Remove the 10 gram weight and introduce pulverized limestone, or other substance that is being tested, until the instrument is immersed to exactly the same point that it occupied with the suspended weight. The reservoir will now contain 10 grams of sample. Connect up the graduated stem and add water, a drop at a time, through the funnel-shaped top, until immersed to the zero point. Raise the hydrometer out of the water and open the stopcock D until the acid drops slowly into the reaction chamber, decomposing the carbonate. As the reaction proceeds the instrument rises slowly and at the conclusion the point on stem at the surface of the water gives the per cent of calcium carbonate equivalent to the carbon dioxide in the sample. This figure is the calcium carbonate equivalent.

A Fahrenheit thermometer accompanies each instrument and is hung inside the floating cylinder. Its reading is taken before and after each determination to allow for any error due to change in temperature. To the figure for calcium carbonate equivalent add 0.5 for each degree rise, or subtract 0.5 for each degree fall in temperature between the two readings.

## VOLUMETRIC METHODS FOR THE DETERMINATION OF CARBON

### Total Carbon. Absorption of Carbon Dioxide in Barium Hydroxide[1]

The carbon dioxide evolved by oxidation of the material by dry combustion with oxygen or by oxidation with chromic sulphuric acid mixture is absorbed in barium hydroxide, free from carbonate, and the precipitated barium carbonate titrated with standard hydrochloric acid.

**Procedure.**— The essential difference in this method from those already described under the gravimetric methods is in the fact that a perfectly clear saturated solution of barium hydroxide is used for absorption of the carbon dioxide in place of caustic potash. Considerable care must be exercised to prevent contaminating the reagent with carbonate. The solution is drawn by suction through a siphon,

Fig. 67. — Victor-Meyer Bulb.

dipping below the surface of the reagent, into the absorption tube, which should be of such construction that the material may readily be poured out. After absorption of the $CO_2$ gas, the apparatus is disconnected and the excess barium hydroxide neutralized with dilute hydrochloric acid (1:4) using phenolphthalein indicator. A few drops of methyl orange are now added and a measured excess of standard hydrochloric acid run in from a burette. After heating to boiling the excess acid is titrated with standard caustic solution, 1 cc. of which is equivalent to 1 cc. of the hydrochloric acid.

$$HCl \times 0.1646 = C.$$

1 cc. N/10 HCl = 0.0022 gram $CO_2$, or 0.0006 gram C.

Note. The method is used in the Omaha laboratory of the Union Pacific Railroad. Dr. N. F. Harriman, Chief Chemist, informed the writer (W. W. Scott), that with care no difficulty is experienced with contamination of the barium hydroxide and excellent results are obtained. The Victor-Meyer bulb is used for holding the barium hydroxide.

### Determination of Carbon Dioxide in a Gas Mixture

See Gas Analysis.

[1] See also article by Cain, J. Ind. Eng. Chem., 6, 465 (1914).

## CYANOGEN

### DETECTION

**Traces of Hydrocyanic Acid.** — To the solution to be tested are added two drops of 10% NaOH and the mixture is evaporated to near dryness. After cooling, a drop of 2% ferrous sulphate is added and the sample allowed to stand in the cold for about fifteen minutes. Now 2–3 drops of strong HCl are added and the solution warmed gently, then cooled. The solution is a blue green if HCN was present in the original sample. 0.000002 g. HCN may be detected.

NOTE. Test for Cyanide. This depends upon the solvent action of HCN upon freshly precipitated HgO in presence of KOH. The filtrate is tested for mercury in an acid solution by addition of $H_2S$. (Hood.)

### VOLUMETRIC DETERMINATION OF HYDROCYANIC ACID [1]

The method depends upon the decolorization of the blue ammoniacal solutions of cupric salts by a soluble cyanide, the reduction to cuprous condition being available for an accurate quantitative estimation of the cyanide.

**Standard Copper Sulphate.** — Twenty-five grams of copper sulphate, $CuSO_4.5H_2O$ are dissolved in a 1000-cc. flask with 500 cc. of distilled water and ammonium hydroxide added until the precipitate that first forms dissolves and a deep blue solution is obtained. Water is now added to make the volume exactly 1000 cc. The cupric solution is standardized by running a portion into a solution containing 0.5 gram pure potassium cyanide, KCN, per 100 cc. of water and 5 cc. of ammonium hydroxide until a faint blue color is evident. Chlorides do not interfere.

**Procedure.** — 0.5 gram of the soluble cyanide is dissolved in 100 cc. of water and 5 cc. strong ammonium hydroxide added. The standard cupric sulphate solution is now added until the blue color is obtained. The cc. required multiplied by the factor of the copper salt in terms of the salt sought gives the weight of that salt in the sample.

[1] J. McDowell, C. N., 1904, p. 221.

### Liebig's Method for Determination of Hydrocyanic Acid. Soluble Cyanides [1]

Silver nitrate reacts with an alkali cyanide in neutral or alkaline solution as follows: $AgNO_3 + 2KCN = Ag(CN)_2K + KNO_3$. The potassium silver cyanide is soluble, hence the precipitate that first forms immediately dissolves on stirring as long as the cyanide is present in excess or in sufficient quantity to react according to the equation. A drop of the silver salt in excess will produce a permanent turbidity; owing to the following reaction:

$Ag(CN)_2K + AgNO_3 = 2AgCN + KNO_3$, the insoluble AgCN being formed.

**Procedure.** — The alkali cyanide contained in a beaker placed over a sheet of black glazed paper, is treated with 4 to 5 cc. of 10% KOH solution and diluted to 100 cc. The liquid is now titrated with standard silver nitrate, with constant stirring, until a faint permanent turbidity is obtained.

One cc. N/10 $AgNO_3$ = 0.013022 gram KCN.

### Determination of Cyanide by Volhard's Method

The method involves Volhard's method for determining halogens, the procedure depending upon the fact that the silver salts of cyanides are insoluble in dilute cold nitric acid solutions.

The neutral cyanide solution is treated with an excess of silver nitrate reagent, and slightly acidified with nitric acid and diluted to a definite volume in a measuring flask. A portion of the solution is now filtered through a dry filter, and a convenient aliquot portion of this is titrated with standard thiocyanate solution, using ferric alum as indicator (see page 523) to determine the silver nitrate present. From this titrate the excess silver nitrate reagent added and that combined with the cyanide ascertained.

1 cc. N/10 $AgNO_3$ = 0.006511 g. KCN or 0.005203 g. CN.

[1] Ann. d. Chem. und Pharm., **77**, p. 102.

## COMPLEX COMPOUNDS — FERRO AND FERRI CYANIDES

### Hydroferrocyanic Acid

One gram of the hydroferrocyanide in 100 cc. of water acidificd with 10 cc. of sulphuric acid is titrated in a casserole with standard potassium permanganate to a permanent pink color. The end-point is poor, so that it is advisable to standardize the permanganate against pure potassium ferrocyanide.

Reaction: $2H_4Fe(CN)_6 + O = H_2O + 2H_3Fe(CN)_6$

One cc. N $KMnO_4$ = 0.3683 gram $K_4Fe(CN)_6$

### Hydroferricyanic Acid

Ten grams of hydroferricyanide are dissolved in water, the solution made alkaline with KOH and heated to boiling and an excess of ferrous sulphate solution added. The yellowish brown ferrid hydroxide turns black with excess of ferrous salt. The solution is diluted to exactly 500 cc. and 50 cc. of a filtered portion titrated with potassium permanganate.

One cc. N $KMnO_4$ = .3292 gram $K_3Fe(CN)_6$.

## CERIUM

**Ce at.wt. 140.25; sp.gr. 6.63, m.p. 623° C. Oxide, $CeO_2$, $C_2O_3$**

The estimation of the rare earths, with the exception of cerium is seldom required as the various elements have found but limited commercial applications. They have all been separated from their native combinations, but only a few have been isolated and many are still believed to be combinations of elements.

Cerium owes its importance to the fact that it enters into the manufacture of Welsbach mantles; in the form of $Ce_2(SO_4)_3$ it is used in the manufacture of aniline black; as oxalate, it is used in medicine, and as metal it used in certain alloys.[1]

### OCCURRENCE

*Minerals:* Monazite,[2] (Ce,La,Di,Th) $PO_4$; Cerite, (Ca,Fe,Y,Zr.) (CeO) $(Ce_2OH)(SiO_3)_3$; Tysonite, (Ce,La,Di)$F_3$; Flocerite, $(Ce,La,Di)_2\ OF_4$; Yttrocerite, $(Y,Er,Ce)F_3.5CaF_2.H_2O$; Parisite, $[(Ce,La,Di)F]_2CaCO_3$.

### DETECTION

The mineral is decomposed and the rare earths are separated from the common base metals as oxalates, these are ignited, then dissolved in HCl or $HNO_3$ and evaporated to dryness. The residue is dissolved in water and evaporated a second time to obtain a neutral solution. This residue is dissolved in water and tested.

Cerous oxalate $Ce_2(C_2O_4)_3.10H_2O$ is precipitated by the addition of oxalic acid to a dilute mineral acid solution of the cerous or ceric salt. The precipitate is white if pure, or pink to cinnamon color in presence of other rare earths.

**Peroxide Test.**— Hydrogen peroxide is added to the solution and then ammonia, drop by drop. A precipitate having the appearence of $Fe(OH)_3$ forms in presence of cerium. The ammonia may be added first and then the peroxide.

Cerium may be detected by the addition of sodium hypochlorite to the solution of a colorless cerous salt. Red ceric hydroxide is precipitated. The test may be confirmed by the chlorine gas evolved when the precipitate is dissolved in hydrochloric acid.

Cerous salts are precipitated by fixed alkalies and are insoluble in excess. Tartaric acid hinders the precipitation.

[1] Automatic lighter contains 35 % Fe and 65 % Ce.

[2] Monazite sand consists of particles of monazite, rutile, thorite, cassiterite, topaz, magnetite, quartz and other heavy minerals. The monazite content varies from a trace to 2–4 percent.

## GRAVIMETRIC ESTIMATION

### Decomposition and Separation of the Rare Earths and Isolation of Cerium

The finely ground mineral (100 mesh or finer) may be frequently decomposed by treating with either hot concentrated hydrochloric acid or sulphuric acid. A fusion with sodium carbonate may be necessary.

When a mineral is digested with hydrofluoric acid, the rare earths are left as insoluble fluorides which must be decomposed by boiling with sulphuric acid to obtain solution.

The difficulty of attack increases in proportion to the amount of tantalic acid present in the sample. Fusion with sodium peroxide is a very quick and energetic method for effecting decompositions of nearly all classes of material. Potassium bisulphate or sodium carbonate may also be used. The following procedure is recommended by J. P. Bonardi.[1]

The powdered mineral is digested with hydrochloric, hydrofluoric or sulphuric acids or aqua regia, (finishing always with sulphuric acid), the solution containing the excess acid is evaporated to copious fumes, carrying the solution down to near dryness with sulphuric acid several times to insure conversion of the phosphate minerals to sulphates. The residue is extracted with ice cold water, acidulated with sulphuric acid, allowing the solution to remain in contact until all basic salts are dissolved. If the mineral carries much titanium, columbium, etc., it is best to extract the residue with nitric acid. The combined filtrates, if nitric acid is present, are evaporated to dryness and the residue taken up with dilute hydrochloric acid. (If a bisulphate fusion or alkali fusion was necessary, extraction with water dissolves the rare earth metals. Silica is removed by evaporation with HCl in the usual way, extracting the residue and filtering off $SiO_2$).

The acid solution containing the rare earths and base metals is saturated with $H_2S$ to remove the second group metals. The $H_2S$ is boiled off in the filtrate and ammonium chloride and ammonium hydroxide added to precipitate the rare earths and the members of the iron group so precipitated. This effects a separation from cobalt, nickel, manganese, zinc, the ammonium carbonate group, the alkalies, and certain of the less common elements of the ammonium sulphide group. The precipitate is washed and then dissolved in dilute hydrochloric acid and the dilution of the solution adjusted so that approximately 1 gram of the rare-earth oxides is contained in 60 cc. and the acidity is not over 0.5 N (approximately 18 grams HCl per liter). The solution is heated to 60° C. and the rare earths (including thorium and cerium) precipitated by the addition of an

[1] U. S. Bureau of Mines.

excess of oxalic acid, sufficient to leave 3 grams of oxalic acid per 100 cc. of the final solution. It is best to allow the solution to stand overnight at 60° C., after which the precipitate is filtered off and thoroughly washed with hot, slightly acidified water. If much foreign metals (zirconium, titanium, etc.) are present in the ore and especially if the presence of phosphates are suspected in the oxalate precipitate, it should be ignited to the oxides, dissolved in hydrochloric acid and a second precipitation made with oxalic acid.

**Separation of Cerium from Other Rare Earths.** — The rare earth oxalates including cerium are ignited, the oxides formed are dissolved in hydrochloric acid. (Addition of a little hydrogen peroxide will hasten the solution of cerium by reduction to the lower oxide; the excess must be removed by boiling.) Sodium hydroxide is added until the hydroxides are completely precipitated, the precipitate is washed on a filter, then transferred to the original beaker in which it was made, 20 cc. of water added, and about 2 grams of sodium hydroxide. Liquid bromine is now added in distinct excess, and the mixture placed on a steam bath until the greater part of the bromine is expelled. The process is repeated three times. Ceric hydroxide remains insoluble while all other cerium earths and the yttrium earths will be found in solution.

Chlorine gas may be used in place of bromine, by passing into the mixture until it no longer reacts alkaline. Iodine may also be used.

**Separation of Thorium from Cerium.** — Thorium is completely separated from cerium and the rare earths by adding a boiling solution of *sebacic acid* to the neutral solution of the rare earths. Thorium sebacate is precipitated as a flocculent precipitate, which is easily filtered. (Ref. T. O. Smith and C. James, J. Am. Chem. Soc., 34, 1912, pp. 281–4.)

Thorium may be removed from cerium by means of *hydrogen peroxide* as follows: The oxalates of the rare earths are ignited, the oxides treated with nitric acid and evaporated to dryness, a little water added and the evaporation repeated. The neutral solution of the nitrates is diluted to 100 cc., 10 grams of ammonium nitrate are added, the solution heated to 60–80° C. and the thorium precipitated by adding 20 cc. of 3% hydrogen peroxide. The gelatinous precipitate, $Th_2O_7.N_2O_5$, is filtered off and washed with 2% ammonium nitrate. Cerium passes into the filtrate. To recover any occluded cerium, the precipitate is dissolved in dilute nitric acid, the solution evaporated to dryness, the residue taken up with a little water and again evaporated to obtain a neutral substance, water is now added, together with ammonium nitrate and hydrogen peroxide as stated above and thorium again precipitated, filtered off and washed. The filtrate contains any occluded cerium, and is added to the first filtrate obtained. Cerium is determined in this solution.

## METHODS

### DETERMINATION OF CERIUM IN PRESENCE OF OTHER RARE EARTHS BY PRECIPITATION AS CERIC IODATE — METHOD OF BRINTON AND JAMES[1]

The method has been found accurate for determining cerium in presence of large amounts of rare earths.

**Procedure.** — To the solution containing the rare earth nitrates (thorium having been previously removed) is added enough concentrated nitric acid to make up $\frac{1}{3}$ of the total solution. At this point this should not exceed 75 cc. The amount of sample taken should contain not over 0.15 gram of ceria, since the precipitate is bulky and the washing is rendered more difficult by the large precipitate. About 0.5 g., very roughly estimated, of solid potassium bromate is added, and when it has dissolved, an amount of potassium iodate which is 10 to 15 times that theoretically required for the estimated ceria present is added in form of the nitric acid solution already given. This reagent is to be slowly added with constant stirring. The precipitate of ceric iodate is allowed to settle in the cold until the supernatant liquid is practically clear, and it is then filtered on a paper of close texture, used for fine substances. The precipitate is brought upon the paper pretty completely, and the beaker rinsed just once with a small amount of the washing solution already described. After draining, but not standing longer than is necessary, the precipitate is carefully rinsed from the paper back into the beaker with more of the washing solution. Any clots should be broken up with a stirring rod, and the mixture well churned. The precipitate is again brought on the same filter in the same way, and allowed to drain. It is then rinsed back into the beaker with hot water, heated to boiling, with constant stirring, and conc. nitric acid is dropped in until the precipitate is completely dissolved. Any unnecessary excess of nitric acid is to be avoided. For about 0.1 g. of ceric oxide from 20 to 25 cc. of acid will usually be required. To this solution about 0.25 g. of potassium bromate is added, and about the same amount of potassium iodate as was used in the first precipitation. This may be used in the form of the regular precipitating reagent, unless the use of this solution would make the volume unduly large, in which case the solid potassium iodate can be dissolved by heating in a small volume of 1 : 2 nitric acid, and thus added. The precipitate is allowed to settle as before, and the perfectly cold mixture is then filtered through the original paper, given one very small washing with the nitric acidiodate washing solution, rinsed back into the beaker once more, well churned, and finally brought on to the paper and washed with 3 small portions of the washing solution. Every trace of the

[1] H. M. P. Brinton and C. James, Jour. Am. Chem. Soc., 41, 7, 1080, July, 1919.

ceric iodate need not be removed from the beaker. The paper with the precipitate is now lifted from the funnel and dropped into the original beaker, taking care to remove any trace of ceric iodate adhering to the glass funnel, either with the upper edge of the filter paper or with a small fragment of another "ashless" filter paper. About 5–8 g. of oxalic acid crystals are now added, and then 50 cc. of water. The covered beaker is heated gently, and its contents are finally boiled until iodine vapors are no longer given off, and all sublimed iodine is vaporized from the cover glass and from the upper edges of the beaker. The cover glass and sides of the beaker are rinsed down with water, and after having stood for several hours the cerous oxalate, mixed with the pulp of the first paper, is filtered, washed with cold water, and ignited in a platinum crucible over the blast lamp. The weight of ceric oxide is obtained by deducting the weight of the two paper ashes.

### DETERMINATION OF CERIUM IN WELSBACH MANTLES — COLORIMETRIC METHOD

Burn off the organic matter and heat with about three times their own weight of $H_2SO_4$ (conc.) on a sand bath. Allow to cool and pour into 20 cc. of water. In twenty-four hours the sulphates are completely dissolved and the solution after neutralizing the excess of acid with ammonia water is precipitated with oxalic acid. The oxalates after settling out are filtered, washed, transferred to a porcelain casserole and digested with nitric acid, a little being added at a time until complete decomposition has taken place. Evaporate to dryness to remove the excess acid. The nitrates of cerium and thorium are dissolved in water and made to volume. Aliquots are then taken and diluted in comparison tubes, 1 cc. $H_2O_2$ (Merck's perhydrol) is added. On adding ammonia water $Th(OH)_4$ is colored orange in proportion to the amount of cerium present. In dilute solutions citric acid prevents the precipitation of the hydroxides and the color can be easily compared with standards containing known amounts.

## SEPARATION OF RARE EARTH OXALATES

Convert into the sulphates by evaporating with sulphuric acid. Dissolve in water and add solid sodium sulphate in excess to the nearly neutral solution.

**(1) Precipitate:**

Th, Ce, La, Pr, Nd, Sa, Eu, Gd, etc., as double sodium sulphates.
Boil with an excess of sodium hydroxide, filter, wash with hot water and dissolve in nitric acid. Treat the nitrates with an excess of zinc oxide and potassium permanganate.

**(3) Precipitate:**

$CeO_2$ and $ThO_2 \cdot MnO_2$ is present is removed by solution in hydrochloric acid and then precipitation of the Ce and Th as double sulphates with sodium.
Precipitate is boiled with an excess of sodium hydroxide, washed with hot water and dissolved in nitric acid. Add ammonia and ammonium oxalate and ammonium acetate.

| Precipitate: | Filtrate: |
|---|---|
| Cerium oxalate. Treat with excess of zinc oxide and solution of potassium permanganate. Cerium oxide precipitates. Dissolve in hydrochloric acid and precipitate *cerium* as oxalate with oxalic acid. | Thorium oxalate is treated with ammonia in excess, ignite. $ThO_2$. |

**(3) Filtrate:**

Saturate the solution with sodium sulphate and wash the precipitate formed with a solution of sodium sulphate.

| Precipitate: | Filtrate: |
|---|---|
| Boil with excess of sodium hydroxide, filter and wash with hot water. Dissolve in a known amount of nitric acid and add an equivalent amount of magnesium nitrate in solution. Evaporate the solution until upon blowing on surface small crystals form. Spray water on surface and allow to crystallize.<br>*Lanthanum* crystallizes 1st, *Praseodymium* crystallizes 2d, *Neodymium* crystallizes 3d *Samarium* crystallizes 4th *Europium* crystallizes 5th *Gadolinium* crystallizes 6th<br>The crystallization is controlled by the spectroscope. The greater number of times the earths are fractionated the purer the product will be. | Combine with filtrate No. 1. |

**(1) Filtrate:**

As double sodium sulphates. Yt, Tb Dy, Ho, Er, Tm, Yb, Sc, etc.
Add oxalic acid in excess to precipitate the earths as oxalates.

**(2) Precipitate:**

As an excess of sulphuric acid and evaporate to form anhydrous sulphates of Yt, Tb, anhyd sulphates of Yt, Yb, Dy, Ho, Er, Tm, Sc, Yb, etc.
Dissolve in cold water and pour over an excess of barium bromate. Stir well and place on the hot water bath. When double decomposition is complete (when the liquid gives no further precipitate with barium bromate solution after diluting and boiling), the mass is filtered and evaporated to crystallization.
*Terbium* crystallizes 1st, *Dysprosium* crystallizes 2d, *Holmium* crystallizes 3d, *Yttrium* crystallizes 4th, *Erbium* crystallizes 5th, *Thulium* crystallizes 6th
The mother liquor is made neutral with ammonia and saturated with potassium sulphate.

| Precipitate | Filtrate: |
|---|---|
| *Scandium.* Potassium Sulphate. | Add oxalic acid. *Ytterbium* is precipitated as oxalate. |

**(2) Filtrate:**

Add to filtrate No. 3.

Table compiled by R. S. Owens.

## CHLORINE

**$Cl_2$, at.wt. 35.46; D. (air), 2.491; m.p. – 101.5°;[1] b.p. – 33.6° C.; oxides, $Cl_2O$, $ClO_2$, $Cl_2O_7$**

### OCCURRENCE

The determination of chlorine is required in a large number of substances. It occurs combined as a chloride mainly with sodium, potassium and magnesium. Rock salt, NaCl, sylvine, KCl, carnallite, $KCl.MgCl_2.6H_2O$, matlockite, $PbCl_2.PbO$; horn silver, AgCl, atacamite, $CuCl_2.3Cu(OH)_2$, are forms in which it is found in nature. Chlorine is determined in the evaluation of bleaching powder. It is estimated in the analysis of water.

### DETECTION

**Free Chlorine.** — The yellow gas is recognized by its characteristic odor. It liberates iodine from iodides; it bleaches litmus, indigo, and many organic coloring substances.

**Chlorides. Silver Nitrate Test.** — In absence of bromides and iodides, which also form insoluble silver salts, silver nitrate precipitates from solutions containing chlorides white, curdy silver chloride, AgCl (opalescent with traces), soluble in $NH_4OH$ (AgBr slowly soluble, AgI difficultly soluble), also soluble in concentrated ammonium carbonate (AgBr is very slightly soluble; AgI is insoluble). Silver chloride turns dark upon exposure to light.

**Free Hydrochloric Acid. Manganese Dioxide, Potassium Permanganate,** and certain oxidizing agents liberate free chlorine gas when added to solutions containing free hydrochloric acid. The gas passed into potassium iodide liberates free iodine, which produces a blue solution with starch.

**Detection in Presence of Bromide and Iodide.** — About 10 cc. of the solution is neutralized in a casserole with acetic acid, adding about 1 to 2 cc. in excess, and then diluting to about 6 volumes with water. About half a gram of potassium persulphate, $K_2S_2O_8$, is added and the solution heated. Iodine is liberated and may be detected by shaking the solution with carbon disulphide, which is colored blue by this element. Iodine is expelled by boiling, the potassium persulphate being repeatedly added until the solution is colorless. Bromine is liberated by adding 2 or 3 cc. of dilute sulphuric acid and additional persulphate. A yellowish-red color is produced by this element. Carbon disulphide absorbs bromine, becoming colored yellowish red. Bromine is expelled with additional persulphate and by boiling. The

volume of the solution should be kept to about 60 cc., distilled water being added to replace that which is expelled by boiling. When bromine is driven out of the solution, the silver nitrate test for chlorides is made. A white, curdy precipitate, soluble in ammonium hydroxide and reprecipitated upon acidifying with nitric acid, is produced, if chlorides are present.

### SUGGESTION FOR THE STUDENT

For the beginner it is advisable to start on a soluble chloride such as sodium chloride, or barium chloride, etc., and determine chlorine by the gravimetric method outlined on page 211. Follow the gravimetric method by Volhard's or Mohr's methods given on pages 214–215. It may be preferred to take up the volumetric procedures after completion of several additional gravimetric methods.

## GRAVIMETRIC DETERMINATION OF CHLORINE

### Preparation and Solution of the Sample

In dissolving the sample the following facts should be borne in mind: Although chlorides are nearly all soluble in water, silver chloride is practically insoluble (100 cc. dissolves 0.000152 gram at 20° C.); mercurous chloride is nearly as insoluble as silver chloride (0.00031 gram); lead chloride requires heat to bring it into solution (in cold water only 0.673 gram soluble per 100 cc. of water). Chlorides of antimony, tin, and bismuth require free acid to keep them in solution. Hydrochloric acid increases the solubility of silver, mercury, lead, antimony, bismuth, copper (Cu′), gold and platinum, but decreases the solubility of cadmium, copper (Cu″), nickel, cobalt, manganese, barium, calcium, strontium, magnesium, thorium, sodium, potassium and ammonium chlorides.

Chlorine gas is most readily dissolved in water at 10° C. (1 vol. $H_2O$ dissolves 3.095 vols. Cl). Boiling completely removes chlorine from water.

Hypochlorites, chlorites, chlorates, and perchlorates are soluble in water.

The chlorine may be present either combined or free. In the combined state it may be present as free hydrochloric acid or as a water-soluble or insoluble salt.

**Water-soluble Chlorides.** — Chlorides of the alkali or alkaline earth groups may be treated directly with silver nitrate upon making slightly acid with nitric acid, the chlorine being determined either gravimetrically or volumetrically according to one of the procedures given later. It is convenient to work with samples containing 0.01 gram to 1 gram of Cl. The sample is dissolved in about 150 cc. of water, made acid with nitric acid with about 5 to 10 cc. in excess of the point of neutralization, should the sample be alkaline. Then the chlorine combined as chloride is determined as directed later.

If the water solution contains a chloride of a heavy metal which forms basic salts (e.g., stannic, ferric, etc., solutions), or which may tend to reduce the silver solution, it is necessary to remove these by precipitation with ammonium hydroxide, or by sodium hydroxide, or potassium carbonate solution. The salt is dissolved in water and acidified with $HNO_3$, adding about 10 cc. in excess, for about 150 cc. of solution. (This excess $HNO_3$ should be sufficient to oxidize substances which would tend to reduce the silver reagent; e.g., $FeSO_4$, etc.) Ammonia solution (free from chloride) is added in sufficient quantity to precipitate the heavy metals iron, manganese, aluminum, etc. The mixture is filtered and the residue washed several times with distilled water. Chlorine is determined in the filtrate by acidifying with $HNO_3$ as directed above.

**Water-insoluble Chlorides.** — The chloride may frequently be decomposed by boiling with sodium carbonate solution. Many of the minerals, however, require fusion with sodium carbonate to prepare them for solution; e.g., apatite, sodalite, etc. Silver chloride may also be decomposed by fusion.

**Silver Chloride.** — The sample is mixed with about three times its weight of $Na_2CO_3$ and fused in a porcelain crucible until the mass has sintered together. The soluble chloride, NaCl, is leached out with water, leaving the water-insoluble carbonate of silver, which may be filtered off. The filtrate is acidified with $HNO_3$ and chlorine determined as usual.

**Chlorine in Rocks.** — The finely ground material is fused with about five times its weight of potassium carbonate. The melt is extracted with hot water, cooled and the solution acidified with nitric acid (methyl orange indicator), and the solution allowed to stand several hours (preferably over night). If silicic acid precipitates, the solution is treated with ammonia and boiled, filtered and the filter washed with hot water. The cooled filtrate is acidified with nitric acid and chlorine determined as usual. If silicic acid does not separate, the addition of ammonia may be omitted and chlorine determined in the solution.

**Free Chlorine.** — Free chlorine may be determined volumetrically according to the procedure given under this section. If it is desired to determine this gravimetrically, a definite amount of the chlorine water is transferred by means of a pipette to a flask containing ammonia solution and the mixture heated to boiling. The cooled solution is acidified with nitric acid and the chloride precipitated with silver nitrate according to the standard procedure.

NOTE. Free chlorine cannot be precipitated directly, as the following reaction takes place: $6Cl + 6AgNO_3 + 3H_2O = 5AgCl + AgClO_3 + 6HNO_3$.

Reaction of chlorine with ammonia: $2Cl + 2NH_4OH = NH_4Cl + NH_4OCl + H_2O$. When the solution is boiled $NH_4OCl$ breaks down, e.g., $3NH_4OCl + 2NH_3 = 3NH_4Cl + N_2 + 3H_2O$.

**Separation of Chlorine and the Halides from the Heavy Metals.** — Halides of the heavy metals are transposed by boiling their solutions with sodium carbonate, the heavy metals being precipitated as carbonates and the halides going into solution as sodium salts.

**Separation of Halides from Silver and from Silver Cyanide.** — The silver salt is treated with an excess of zinc and sulphuric acid, the metallic silver and the paracyanogen filtered off, and the halides determined in the filtrate.

NOTE. See the method of determining chlorine, bromine, and iodine in presence of each other at end of this chapter.

## SILVER CHLORIDE METHOD

The procedure is based on the insolubility of silver chloride in dilute nitric acid solution, the following reaction taking place, M representing a monatomic element:

$$M.Cl + AgNO_3 = M.NO_3 + AgCl$$

From the equation it is evident that 35.45 grams of chlorine require 169.9 grams of silver nitrate. In practice it is best to add about 20% excess of the silver salt.

Equivalents: 1 gram Cl, 4.79 grams $AgNO_3$, 3.043 grams Ag.

**Reagents.** — *Silver Nitrate Solution.* — Make up a solution containing 4.8 grams $AgNO_3$ per 100 cc. of distilled water, or dissolve 3.05 grams of silver foil in 10 cc. of dilute nitric acid (1 : 1.6) and make up to 100 cc. 1 cc. of this reagent will precipitate 0.01 grams of chlorine, or 0.0404 + grams AgCl.

*Dilute Nitric Acid.* — One vol. $HNO_3$ to 1.6 vols. $H_2O$ (dist.).

**Procedure.** — *Soluble Chlorides.* — *Preparation of the Solution.*

1. Weigh 0.4 to 0.5 grams of the salt on a watch glass or in a weighing bottle and transfer to a beaker or an Erlenmeyer flask.

2. Dissolve in 100 cc. of water and add 2 cc. of dilute nitric acid.

3. *Precipitation.* — Calculate roughly the cc. of the silver nitrate reagent that are required to precipitate the chlorine in the sample. If it is an unknown, consider the chlorine in the material to be about 50%. Run the determination in duplicate. The first will be a guide to the amount of silver nitrate solution required.

4. Add the silver nitrate from a burette, drop by drop, to approximately the quantity calculated to be necessary, stirring the solution during the addition. Allow the precipitate to settle and add a few more drops of the reagent, and continue the addition as long as a precipitate forms with the reagent. Now add about 20% in excess.

5. Heat to boiling, covering the beaker with a watch glass.

6. If the solution is still cloudy stir vigorously. If the solution is in an Erlenmeyer flask the mixture may be shaken. This will cause the finely divided silver salt to coagulate so that the solution will settle out clear. Avoid exposing the precipitate to strong light, as this will cause the exposed surface to decompose into the subchloride $Ag_2Cl$ and liberate chlorine.

7. *Filtration.* — Two processes are commonly practiced.

*Filter paper method.* — Decant the clear solution into a filter. Test the filtrate to be sure all chlorine has been precipitated by adding a drop or so of silver nitrate solution. Wash the precipitate in the beaker twice by decantation and then transfer to the filter and wash until free of chlorides. The wash water should contain 1 cc. of nitric acid per 100 cc. of distilled water.

8. Dry the filter with its contents at 105° C either in the funnel in which the operation was conducted or on a watch glass. It is advisable to protect the sample from dust by placing a large filter over the material.

9. Remove as much of the precipitate as possible from the filter, placing the silver chloride on a 4 inch square of glazed paper.

10. Ignite the filter allowing the ash to drop into a weighed porcelain crucible. Add a drop of nitric acid and a drop of hydrochloric acid to react with any reduced silver. Place the silver salt (on the glazed paper) in the crucible and gently ignite until the chloride begins to melt. If the AgCl appears dark, moisten with HCl and again apply heat to expel the free acid.

11. Cool in a desiccator.

12. Weigh as silver chloride. (wt. crucible + AgCl) − wt. crucible = wt. AgCl. The compound contains 24.74% of chlorine.

$$AgCl \times 0.2474 = Cl$$

13. Calculate the per cent chlorine from the weight of sample taken.

*Gooch crucible method.* — 8[a]. Prepare a Gooch crucible filter with a moderately thick asbestos mat and wash thoroughly with distilled water containing 1 cc. nitric acid per 100 cc. of water.

9[a]. Dry the crucible with mat in an oven at 100° C, then heat gently over a free blue flame. Cool in desiccator and weigh.

10[a]. Wash the silver chloride, first by decantation, then transfer to the Gooch crucible, which has been placed in position on a suction flask. (Consult directions for the preparation of a Gooch and the method of filtration under "Laboratory Apparatus and Manipulations" in the introductory chapter.) Gentle suction is applied and the precipitate is washed free of chloride by repeated additions of the wash water containing the nitric acid.

11[a]. Place the crucible in an oven for 15 minutes or more and dry at 105° C. Now place over a free blue flame and heat until the silver begins to melt. Cool in a desiccator.

12[a]. Weigh. The weight in excess of that due to the crucible is due to silver chloride.

13[a]. Calculate percent chlorine as stated under the "filter paper method," 12 and 13.

NOTE. The silver chloride may be removed from the crucible by adding a piece of zinc and dilute sulphuric acid to the residue.

**Chlorine in Ores and Cinders.** — One hundred grams of the finely ground ore or cinder are placed in a 500-cc. flask, containing 300 cc. of strong sulphuric acid (Cl-free). The flask is shaken to mix the sample with the acid and then connected with an absorption apparatus, containing distilled water or dilute caustic solution. The sample is gradually heated, the distillation flask resting upon a sand bath. After two hours, which is sufficient to expel all the chlorine, as hydrochloric acid, the contents of the absorption tubes are filtered, if free sulphur is present (sulphide ores), nitric acid added and the filtrate brought to boiling to oxidize any $SO_2$ that may be present. Chlorine is precipitated according to the standard procedure.

During the run the distilling flask should be shaken occasionally to prevent caking. Suction applied at the absorption end of the apparatus and a current of air swept through the system aids in carrying over the HCl into the water or NaOH.

## VOLUMETRIC METHODS

### DETERMINATION OF CHLORINE IN ACID SOLUTION, SILVER THIOCYANATE FERRIC ALUM METHOD — VOLHARD'S METHOD

The method is applicable to titration of chlorine in acid solutions, a condition frequently occurring in analysis, where the Silver-Chromate Method of Mohr cannot be used.

Copper (below 60%), arsenic, antimony, cadmium, bismuth, lead, iron, zinc, manganese, cobalt, and nickel, do not interfere, unless the proportion of the latter metals is such as to interfere by intensity of the color of their ions.

**Preparation of Special Reagents.**— *N/10 Ammonium or Potassium Thiocyanate Solution.* — About 8 grams of ammonium or 10 grams of potassium salt are dissolved in water and diluted to one liter. The solution is standardized by titration against the N/10 silver nitrate solution. It is advisable to have 1 cc. of the thiocyanate equivalent to 1 cc. of the silver nitrate solution.

*N/10 Silver Nitrate.* — This solution contains 10.788 grams Ag or 16.989 grams $AgNO_3$ per liter. If pure metallic silver is taken, the required weight is dissolved in nitric acid and made to 1000 cc. The solution is adjusted to exact decinormal strength by standardizing against an N/10 sodium chloride solution, containing 5.846 grams of pure NaCl per liter.

*Ferric Indicator.* — Saturated solution of ferric ammonium alum, (or ferric sulphate), is made by dissolving 10 grams of salt per 100 cc. and adding a few drops of sulphuric acid to clear the solution.

*Pure Nitric Acid.* — This should be free from the lower oxides of nitrogen. Pure nitric acid is diluted to contain about 50% $HNO_3$, and boiled until perfectly colorless. Keep in a dark bottle.

**Procedure.** – To the solution, containing 0.003 to 0.35 gram chlorine in combination as a chloride, is added sufficient of the pure $HNO_3$ to make the solution acid and about 5 cc. in excess. To the solution, diluted to about 150 cc., is added an excess of standard silver nitrate reagent. The precipitated AgCl is filtered off and washed free of silver nitrate. The filtrate and washings are combined and titrated with standard thiocyanate.[1]

The filtrate from the precipitated chloride is treated with 5 cc. of the ferric solution,[2] and the excess silver determined by addition of the thiocyanate until a permanent reddish-brown color is produced. Each addition of the reagent will produce a temporary reddish-brown color, which immediately fades as long as silver uncombined as thiocyanate remains. The trace of excess produces ferric thiocyanate, the reddish-brown color of this compound being best seen against a white background. From this titration the chloride is ascertained.

One cc. N/10 $AgNO_3$ = 0.00355 gram Cl or 0.00585 gram NaCl.

## VOLUMETRIC DETERMINATION OF CHLORINE AS CHLORIDE IN A NEUTRAL SOLUTION, SILVER CHROMATE METHOD, MOHR'S METHOD

The method, worked out by Fr. Mohr, is applicable for determination of chlorine in water or in neutral solutions containing small amounts of chlorine; the element should be present combined as a soluble chloride. Advantage is taken of the fact that silver combines with chlorine in presence of a chromate, $Ag_2CrO_4$ being decomposed as follows: $Ag_2CrO_4 + 2NaCl = 2AgCl + Na_2CrO_4$. When all the chlorine has gone into combination as AgCl, an excess of $K_2CrO_4$ immediately forms the red $Ag_2CrO_4$, which shows the reaction of $AgNO_3$ with the chloride to be complete.

**Reagents.** — *Tenth Normal Silver Nitrate Solution.* — Theoretically 16.989 grams $AgNO_3$ per liter are required. In practice 17.1 grams of the salt are dissolved per 1000 cc. and the solution adjusted against an N/10 NaCl solution containing 5.846 grams NaCl per liter.

*Potassium Chromate.* — Saturated solution.

**Procedure.** — To the neutral solution (made so, if necessary, by addition of nitric acid or ammonium hydroxide), are added 2 or 3 drops of the potassium chromate solution. A glass cell[3] (or a 50 cc. beaker) is filled to about 1 cm. in depth with water tinted to the same color as the solution being titrated. The cell is placed on a clear glass plate half covering the casserole containing the sample. The standard silver solution is now added to the chloride solution from a burette until a faint blood-red tinge is produced, the red change being easily detected by looking through the blank, colored cell.

One cc. N/10 $K_2CrO_4$ = 0.003546 gram Cl.

NOTES. Chlorides having an acid reaction ($AlCl_3$) are treated with an excess of neutral solution of sodium acetate and then titrated with silver nitrate.

Elements whose ions form colored solution with chlorine are precipitated from the solution by sodium hydroxide or potassium carbonate, and the filtrate, faintly acidified with acetic acid, is titrated as usual.

[1] Time is saved by filtering, through a dry filter paper, only a portion of the mixture made to a definite volume, and titrating an aliquot portion. The first 10 to 15 cc. of the filtrate are rejected.

[2] Upon addition of the ferric solution no color should develop. If a reddish or yellowish color results, more nitric acid is required to destroy this. The amount of nitric acid does not affect results when within reasonable limits.

[3] Depré, Analyst, **5**, 123; also, Systematic Handbook of "Volumetric Analysis," F. A. Sutton.

### VOLUMETRIC DETERMINATION OF FREE CHLORINE

The determination depends upon the reaction $Cl + KI = KCl + I$, The iodine liberated by the chlorine is titrated with $Na_2S_2O_3$ and the equivalent Cl calculated.

**Procedure.**—A measured amount of the chlorine water is added to a solution of potassium iodide in a glass-stoppered bottle by means of a pipette, the delivery tip of which is just above the surface of the iodide solution. The bottle is then closed and the contents vigorously shaken. The liberated iodine is titrated with tenth-normal sodium thiosulphate ($2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$). When the yellow color of the iodine has become faint, a little starch solution is added and the titration completed to the fading out of the blue color.

One cc. N/10 $Na_2S_2O_3$ = 0.003546 gram Cl.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Evaluation of Bleaching Powder for Chlorine

When chloride of lime is treated with water, it is resolved into calcium hypochlorite, $Ca(OCl)_2$, and calcium chloride, $CaCl_2$. The calcium hypochlorite constitutes the bleaching agent. The technical analysis is confined to the determination of available chlorine, which is expressed as percentage by weight of the bleaching powder.

**Procedure.** — Ten grams of the sample are washed into a mortar and ground with water, the residue allowed to settle and the supernatant liquor poured into a liter flask. The residue is repeatedly ground and extracted with water until the whole of the chloride is transferred to the flask. The combined extracts are made up to 1000 cc.

To 50-cc. portions (0.5 gram) of the solution, 3 to 4 grams of solid potassium iodide and 100 cc. of water are added and the solution acidified with acetic acid. Iodine equivalent to the available chlorine is liberated. This is titrated with N/10 arsenious acid. 1 cc. = 0.00355 g. Cl. Multiply by 200 = % Cl.

### Chlorine in Cement, Copper, and Copper Ores

If the material contains very little silver the following method is applicable in laboratories equipped with apparatus for furnace assaying.

Ten grams of the finely ground sample placed in an 800 cc. beaker are treated with 600 cc. water, 100 cc. nitric acid (free from iodic acid) and the mixture brought to boiling by gentle heating. After filtration and thorough washing, the insoluble residue is treated repeatedly with additional water and acid, of the above proportion, until a test of the filtrate with silver nitrate indicates complete extraction of the soluble chloride. The combined filtrates are treated with a slight excess of silver nitrate and chloride of silver precipitated and determined in the usual way.

On a separate 10 gram sample an assay of silver is made and the equivalent weight of chloride calculated. This equivalent is added to the weight of silver chloride obtained in the extract. The percent of chlorine is calculated from this result by the formula. (Wt. AgCl. $\times$ .2474 $\times$ 100) $\div$ 10 = gram Cl.

### Determination of Chlorine, Bromine, and Iodine in a Mixture

**Procedure.** — The halogens are precipitated with an excess of silver nitrate, filtered onto asbestos or glass wool, washed, dried, and weighed as total halogens as silver salts. A second portion is precipitated and the moist, washed silver salts (0.3 to 0.4 gram) are treated with a solution of 2 grams of potassium dichromate in 30 cc. of concentrated sulphuric acid at 95° C., and digested for thirty minutes. By this procedure the iodine is oxidized to hydriodic acid ($HIO_3$) and chlorine together with bromine is liberated in form of the free halogen. Toward the end of the reaction a stream of air is led through the solution to remove any chlorine and bromine. This is now diluted to 300 to 400 cc., filtered, and the hydriodic acid reduced by adding, drop by drop, with constant stirring, a concentrated solution of sodium sulphite, $Na_2SO_3$, until a faint odor of $SO_2$ remains after standing ten minutes. (Under certain conditions an excess may result in a partial reduction of the silver iodide.) The precipitated silver salt is filtered, washed with hot, dilute nitric acid, dried and weighed as AgI. The filtrate containing the silver, formerly with the chlorine and bromine, is treated with potassium iodide in sufficient amount completely to precipitate the silver as AgI. This is filtered, washed and weighed. From the three weights the chlorine, bromine and iodine can be easily calculated.

In France the strength is given in Gay-Lussac degrees, e.g., liters of gas evolved by 2 kilograms of bleaching powder, 0° C. and 760 mm. 100° = 31.78 % Cl.

## CHROMIUM

**Cr, at.wt. 52.0; sp.gr. 6.92; m.p. 1520°; b.p. 2200° C; oxides, $CrO_2$; $Cr_2O_3$, $CrO_3$**

### OCCURRENCE

The element occurs in nature only in combined form.

Chrome iron or chromite, crocoite, slags; chromic oxide (chrome green) in pigments; chromates and dichromates; chrome steel and ferrochrome are substances in which chromium is determined.

**Minerals.** — *Chromite*, Chrome Iron, $FeO.Cr_2O_3$, sometimes with $Al_2O_3$ and MgO. Massive black, resembles magnetite; opaque, metallic to submetallic; brittle; dark brown streak, hardness 5.5. Associated with serpentine, mechanically intermixed, giving rise to yellow and green spots or streaks.

*Crocoite*, $PbCrO_4$, hyacinth-red mineral (like $K_2Cr_2O_7$), granular, columnar, or monoclinic crystals; orange streak; hardness 2.5–3.

### DETECTION

Chromium is precipitated by hydrogen sulphide and ammonium hydroxide as bluish-green, $Cr(OH)_3$, along with the hydroxides of iron and aluminum (members of previous groups having been removed). The chromic compound is oxidized to chromate by action of chlorine, bromine, sodium peroxide, or hydrogen peroxide added to the substance containing an excess of caustic alkali. The chromate dissolves and is thus separated from iron, which remains insoluble as $Fe(OH)_3$. The alkali chromates color the solution yellow.

**Barium acetate or chloride** added to a neutral or slightly acetic acid solution of a chromate precipitates yellow barium chromate, $BaCrO_4$. Addition of ammonium acetate to neutralize any free inorganic acid aids the reaction.

**Lead acetate** produces a yellow precipitate with chromates, in neutral or acetic acid solutions.

**Mercurous nitrate or silver nitrate** gives red precipitates.

**Hydrogen peroxide** added to a chromate and heated with an acid, such as sulphuric, nitric, or hydrochloric, will form a greenish-blue colored solution. Chromates are reduced by hydrogen peroxide in acid solution, the action being reversed in alkaline solution.

**Reducing agents, hydrogen sulphide, sulphurous acid, ferrous salts, alcohol** form green chromic salts in acid solution.

**Ether** shaken with a chromate to which nitric acid and hydrogen peroxide are added, is colored a transient blue.

$$HCrO_4 + 3HNO_3 = Cr(NO_3)_3 + 2H_2O + O_2.$$

The powdered mineral, containing chromium, when fused with sodium carbonate and nitrate, produces a yellow colored mass.

## METHODS FOR THE DETERMINATION OF CHROMIUM

### Preparation and Solution of the Sample

Although powdered metallic chromium is soluble in dilute hydrochloric or sulphuric acid, it is only slightly soluble in dilute or concentrated nitric acid. It is practically insoluble in aqua regia and in concentrated sulphuric acid. Chrome iron ore is difficult to dissolve. It is important to have the material in finely powdered form to effect a rapid and complete solution of the sample. An agate mortar may be used to advantage in the final pulverizing of the substance.

Chromium is one of the most refractory of the metals. It oxidizes slowly on heating. The element has three valences; the divalent chromium is basic in character and forms chromous compounds with acids; the trivalent form, more commonly known, is also basic and forms chromic salts with acids; the hexavalent form, obtained by oxidation of a chromic salt in alkaline solution, is acidic in character and combines with bases to form chromate salts. Chromates are reduced in acid solutions by reducing agents, while they are formed in alkaline solutions by oxidation.

Examples. $CrCl_3$ chromic chloride. $K_2CrO_4$ potassium chromate.

**General Procedures for Decomposition of Refractory Materials Containing Chromium.** — The following fluxes may be used:

*A.* Fusion with $KHSO_4$ and extraction with hot dilute HCl. The residue fused with $Na_2CO_2$ and $KClO_3$, 3 : 1, or fusion with soda lime and $KClO_3$, 3 : 1.

*B.* Fusion with $NaHSO_4$ and NaF, 2 : 1.

*C.* Fusion with magnesia or lime and sodium or potassium carbonates, 4 : 1.

*E.* Fusion with $Na_2O_2$, or NaOH and $KNO_3$, or NaOH and $Na_2O_2$. Nickel, iron, copper, or silver crucibles should be used for *E.* Platinum may be used for *A*, *B*, or *C*.

**Special Procedures. — Materials High in Silica.** — The finely ground sample, 1 to 2 grams, is placed in a platinum dish and mixed with 2 to 5 cc. of concentrated sulphuric acid (1.84), and 10 to 20 cc. of strong hydrofluoric acid added. The solution is evaporated to small volume on the steam bath and to $SO_3$ fumes on the hot plate. Sodium carbonate is added in sufficient amount to react with the free acid, and then an excess of 5 to 10 grams added and the mixture heated to fusion and kept in molten condition for half an hour. From time to time a crystal of potassium nitrate is added to the center of the molten mass until 1 to 2 grams are added. (*Caution.* Platinum is attacked by $KNO_3$, hence avoid adding a large amount at any one time.) Chromium and aluminum go into solution in the flux, but iron is thrown out as $Fe(OH)_3$. The cooled fusion is extracted with hot water and filtered from the iron residue. Chromium is in solution together with aluminum. If much iron is present it should

be dissolved in a little hydrochloric acid and the solution poured into boiling 10% solution of potassium hydroxide, the cooled solution + $Fe(OH)_3$ precipitate is treated with hydrogen peroxide or sodium peroxide to oxidize any chromium that may have been occluded by the iron in the first precipitate. The mixture is again filtered and the combined filtrates examined for chromium.

NOTE FOR THE STUDENT. Determine chromium in a soluble chromate by the potassium iodide method as given on page 224. When familiar with this procedure determine chromium in a chrome iron ore or in steel following the directions under "Sodium Peroxide Fusion" or the "Method for Solution of Iron and Steel." The volumetric methods are generally preferred in the determination of chromium.

**Sodium Peroxide Fusion. — Chrome Iron Ores.** — Half to 1 gram of the finely pulverized ore is placed in an iron crucible (25–50 cc.) and mixed with about 5 grams of sodium peroxide. (Fresh peroxide is best.) The mass is gently heated over a Bunsen burner until it melts and the fusion kept at low red heat for about ten minutes, revolving the crucible to avoid overheating and melting of the vessel. If the melt is not clear additional peroxide (1-2 grams) should be added and the heating continued for a few minutes.

On cooling, the crucible with the fusion is placed in a casserole containing about 150 cc. of distilled water. The crucible is upset in the water and the casserole covered until the violent action has subsided. The crucible is washed out and removed and the solution boiled to remove the excess of peroxide.

To the solution is added sufficient ammonium carbonate to neutralize the greater part of the strong alkali (which would otherwise dissolve the filter) and the solution filtered, preferably by suction using a perforated plate with filter covered by a thin layer of paper pulp, in an ordinary funnel. The solution contains the chromium.

Small amounts of chromium may remain in the residue. This is dissolved in dilute sulphuric acid added to the filter. (If any black particles remain, the filter should be ignited and the ash fused with peroxide as directed above, using relatively smaller amounts of reagent and water. The extract is added to the chromium solution.) The acid solution is nearly neutralized with sodium carbonate and sodium peroxide added until strongly alkaline. The solution is boiled to decompose the peroxide, ammonium carbonate added as stated above and the solution filtered. This is combined with the main solution containing the chromium.

If the gravimetric methods are to be followed the solution containing chromium is acidified with nitric acid and the directions observed as given under the special method chosen.

If the iodide or ferrous sulphate methods are chosen for a volumetric determination of chromium the alkaline solution is acidified according to directions given under the method that is to be followed.

**Method for Solution of Iron and Steel.** — One gram of steel is dissolved in 20 cc. of dilute sulphuric acid, 1 : 3. When the evolution of hydrogen from the metal has subsided and no further action is evident nitric acid is added drop by drop until the iron is oxidized, about 5 cc. of $HNO_3$ should be ample. The solution is now boiled until free of nitrous fumes and to the hot solution is added drop by drop a strong solution of potassium permanganate in just sufficient amount to form a permanent brown precipitate of $MnO_2$. A large excess is to be avoided. If the solution is slightly pink, it is boiled until the pink color disappears. The solution is cooled and filtered through an asbestos filter, using suction. (A Gooch crucible is satisfactory.) Chromium is determined in the solution by the ferrous sulphate method according to directions given under this method.

It is advisable to treat the residue on the filter with dilute sulphuric acid containing a little ferrous sulphate. If any dark colored residue remains the decomposition of the ore has not been complete and this residue must be again treated with sulphuric and nitric acids as stated in the procedure above. The extract is added to the main solution.

**Separation of Chromium, Iron, and Aluminum.** — If chromium has been fused with sodium peroxide or carbonate containing a little potassium nitrate, and the fusion extracted with boiling water, most of the chromium goes into solution as a chromate, together with alumina, but some of the chromium is occluded by $Fe(OH)_3$. If the amount of the iron precipitate is appreciable, and warrants the recovery of occluded chromium, it is dissolved in hydrochloric acid and the iron reprecipitated by pouring into a solution of strong sodium hydroxide. Before filtering off the iron hydroxide, a little $H_2O_2$ is added to oxidize the $Cr_2O_3$, if accidentally present, and the solution boiled and filtered. The combined filtrates will contain all of the chromium and aluminum.

If chromium is present as a chromic salt, instead of a chromate, it is oxidized to the higher form, by adding peroxide ($H_2O_2$ or $Na_2O_2$) to the alkaline solution. Bromine added to this solution or chlorine gas passed in will accomplish complete oxidation.[1] It must be remembered that in acid solutions hydrogen peroxide, sodium peroxide, or nitrites will cause reduction of chromates to chromic salts (exception, see method for solution of steel), so that these should be boiled out of the alkaline solution before making decidedly acid with hydrochloric or sulphuric acids. Since these are difficult, if not impossible, to completely expel from an alkaline solution, after boiling the strongly alkaline solution, dilute sulphuric acid is added until the solution acquires a permanent brown color (nearly acid), acid potassium sul-

[1] Br. may be added and then NaOH to oxidize Cr and precipitate $Fe(OH)_3$. Chromic oxide and most of its compounds, except chrome iron stone, may be decomposed by conc. $HNO_3 + KClO_3$ (added in small portions). M. Groger, Zeitsch. Anorg. Chem., 81, 233–242, 1913.

phate, $KHSO_4$, is added, and the boiling continued.[1] This will decompose the bromates and expel bromine, etc., but will not cause the reduction of the chromate, as would a strong acid solution.

**Separation of Chromium from Aluminum.** — This separation is necessary if chromium is to be precipitated as $Cr(OH)_3$. The sodium chromate and aluminate solutions are made slightly acid with nitric acid and then faintly alkaline with ammonium hydroxide, $Al(OH)_3$ is precipitated and chromium remains in solution as a chromate. The separation is not necessary if chromium is to be determined by the volumetric procedures in acid solution.

[1] See Separations.

## GRAVIMETRIC METHOD FOR THE DETERMINATION OF CHROMIUM

### PRECIPITATION OF CHROMIC HYDROXIDE AND IGNITION TO $Cr_2O_3$ [1]

Chromium present as a chromic salt in solution, free from iron and aluminum or elements precipitated as hydroxides, is thrown out of solution by $NH_4OH$ as $Cr(OH)_3$, the precipitate ignited to the oxide, $Cr_2O_3$, and so weighed. The presence of hydrochloric acid or sulphuric acid does not interfere.

**Reduction.**— If the chromium is already present as the chromic salt, free from iron and alumina, it may be precipitated directly as the hydroxide by addition of ammonia; otherwise, if present as the chromate, as is the case when a separation from iron and alumina has been necessary, and in cases where the chromium has been brought into solution by fusion with an oxidizing reagent, reduction is necessary. This is accomplished by passing $SO_2$ or $H_2S$ into the slightly acid solution of the chromate, or by adding alcohol to the hydrochloric acid solution and boiling until the solution appears a deep grass green. Twenty cc. of alcohol for every 0.1 gram of Cr has been found to be ample for this reduction. The $SO_2$ or $H_2S$ should be expelled from solution by boiling, in case either has been used for reduction of the chromate.

**Precipitation. Ammonium hydroxide or ammonium sulphide are added in slight excess and the solution boiled for about ten minutes.**— The solution should be slightly alkaline (litmus), otherwise a few drops of ammonia should be added, but not a large excess; the solution will then settle out clear. A cloudy solution results from prolonged boiling when the solution has become acid; on the other hand, a large excess of ammonia will prevent complete precipitation of chromium and the filtrate will be colored pink or violet. *The chromic hydroxide is filtered.* Since the precipitate is apt to be gelatinous it is advisable to wash two or three times by decantation and several times on the paper. The well-drained precipitate and filter is ignited wet in a porcelain or platinum crucible, first over a low flame until the paper has been charred, then over a strong gas flame for about thirty minutes, and finally a blast heat for five minutes. The green residue is weighed as $Cr_2O_3$[2]

$$Cr_2O_3 \times 0.6846 = Cr.$$

[1] It is advisable to take such a weight of sample that the ignited $Cr_2O_3$ does not exceed 0.5 gram in weight.

[2] $Cr_2O_3$, *mol.wt.*, 152; *sp.gr.*, 5.04; *m.p.*, 2059° C.; insol. in $H_2O$, slightly sol. in acids, dark green hexagonal.

## VOLUMETRIC METHODS

### Potassium Iodide Method for Determination of Chromium

The procedure depends upon the fact that chromium, present as a chromate, is reduced in acid solution by the addition of potassium iodide, the liberated iodine being titrated by standard thiosulphate. The reactions taking place may be represented as follows :

(*a*) $2CrO_3 + 6KI = Cr_2O_3 + 3K_2O + 6I$
(*b*) $I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$

The presence of large quantities of Ca, Ba, Sr, Mg, Zn, Cd, Al, Ni, Co, $H_2SO_4$, cold dilute HCl does not interfere.

**Reagents :**

N/10 Sodium Thiosulphate
Starch Solution
Potassium Iodide, 50% solution
Potassium Acid Sulphate 30% solution

**Procedure.** — 1. *Solution of the sample.* — The methods for decomposition have been given under Preparation and Solution of the Sample, 0.5–1.0 gram of the finely divided chrom iron-ores being preferably decomposed by the peroxide fusion in an iron crucible, chrome steels being decomposed by acid treatment with strong sulphuric acid, nitric acid followed by potassium permanganate. Iron of the steel sample should now be removed by making the solution alkaline. Filtration is accomplished, preferably by suction, using either a Gooch crucible, or a perforated porcelain plate in a funnel with a small filter to fit the plate. See details under Preparation and Solution of the sample. After washing the residue at least five times, proceed as follows:

2. The filtrate contains the chromate freed from iron and other impurities which would interfere in an iodide treatment. Nearly neutralize the solution with dilute sulphuric acid or hydrochloric acid in a flask of about a liter capacity. If any peroxide is suspected to be still present the solution must be boiled at this stage. If this has been removed in the preliminary treatment for obtaining the solution, make the solution slightly acid. The color will deepen to an orange color when it becomes acid. A piece of litmus paper dropped into the flask will act as indicator. Now add about 25 cc. excess of hydrochloric acid (1 : 1).

3. Cool the solution and to the *cold* solution add 2 to 5 cc. of the 50% potassium iodide reagent. There should be present about 2 cc. of the reagent for 0.05 gram of chromium.

4. Titrate the liberated iodine with standard thiosulphate reagent until the brown color becomes faint. Now add about 5 cc. of the starch solution and continue the titration, very cautiously, drop by

drop, until the color due to the starch just disappears with an added drop of the thiosulphate. The liquid will become a clear bluish green tint at this stage, the depth of the color being governed by the amount of chromium present.

5. If N/10 thiosulphate reagent is used, 1 cc. = 0.001733 g. of Cr. Multiply by the factor and calculate the per cent of chromium present.

Notes. In the reduction of chromium it is evident that for every two molecules of chromium, three molecules of oxygen are removed, hence a gram molecular weight, namely 52 grams of chromium per liter is equivalent to $1\frac{1}{2}$ moles of oxygen or 24 grams. Now since 8 grams of oxygen per liter is a normal solution of available oxygen, it is evident that $\frac{1}{3}$ the molecular weight of chromium per liter would be its equivalent, i.e. 17.33 grams or 0.01733 g. Cr. per cc.

Potassium iodide is acted upon by an oxidizing agent as follows:

$$2KI + O = K_2O + 2I$$

Hence in the reduction of $2CrO_3$ to $Cr_2O_3$ we have the reaction given on the previous page in the introduction of the method. 3I are liberated for each atom of Cr.

In place of using a normality solution of thiosulphate A. H. Low suggests the following:

"*A.* The sodium thiosulphate solution used for copper may be employed, in which case the copper value multiplied by 0.2727 = the chromium value. This solution is usually inconveniently weak for chrome iron ore. It is better to prepare a solution containing about 36 grams of the crystallized sodium thiosulphate per liter (with about 5 grams of NaOH added to preserve it). The iodine liberated by the permanganate is equivalent to a certain amount of chromium. This is determined by multiplying the Fe value of the amount of permanganate run in by 0.3105. Titrate this iodine with the thiosulphate solution as described above. Divide the corresponding amount of chromium by the cc. of thiosulphate required, to obtain the value of 1 cc. in chromium. 1 cc. will be found to be equal to about 0.5 % of chromium, on the basis of 0.5 gram of ore taken.

*B.* The thiosulphate may also be standardized against pure potassium dichromate. On the 0.5 gram basis, 0.283 gram of $K_2Cr_2O_7$ = exactly 20 % of chromium. Weigh this amount of powdered salt into a flask of a liter capacity, add about 400 cc. of cold water and about 30 cc. of 1 : 1 HCl. Cool under the tap, add 2 grams of KI, or 4 cc. of a 50 % solution, and titrate with the thiosulphate. Divide the 20 % of chromium present by the number of cc. of thiosulphate used to find the percentage value of 1 cc."

Normal or tenth normal thiosulphate is commonly employed in a number of determinations. Molecular weight $Na_2S_2O_3.5H_2O$ = 248.20. 25 grams per liter are generally taken for N/10 solutions and the reagent standardized against pure iodine (see under the chapter on Iodine).

Sodium peroxide is generally used for oxidation of chromium. The solution is now neutralized with acid, the iodide added and 10 cc. of strong HCl. The liberated iodine is immediately titrated.

If desired, stronger solutions of titration reagents may be used, and consequently larger samples taken. A normal sol. of $Na_2S_2O_3$ may be used to advantage with 1 gram samples of chromium salts or hydrates, where Cr exceeds 10 percent.

Sutton recommends for every 0.5 gram $K_2Cr_2O_7$ present to add .5 gram KI, and 1.8 grams $H_2SO_4$ per 100 cc. of solution. If more $K_2Cr_2O_7$ is present, increase the KI and $H_2SO_4$, but not the water.

If desired, a normal solution of thiosulphate may be used with one gram sample of chromium salts or hydroxides, when the chromium present exceeds 10 percent.

## VOLUMETRIC DETERMINATION BY REDUCTION OF THE CHROMATE WITH FERROUS SALT

The determination may be made in the presence of ferric iron and alumina, hence the method is suitable for the determination of chromium in iron and steel and aluminum products. Hydrochloric and sulphuric acids do not interfere. If hydrochloric acid is present the titration with potassium dichromate to oxidize the excess of ferric salt is necessary. If this acid is absent either the permanganate or dichromate reagents may be used.

The method depends upon the reduction of chromates in solution by addition of a ferrous salt in known amount in the form of a solution in excess of that required to reduce the chromate. The excess of the ferrous solution is now determined by titration with a standard solution of potassium dichromate or permanganate. The reactions occur as follows:

*Reactions:*

(*a*) $2\ CrO_3 + 6\ FeO + Xs\ FeO = Cr_2O_3 + 3\ Fe_2O_3 + Xs\ FeO$

(*b*) Xs FeO is titrated with $KMnO_4$ or $K_2Cr_2O_7$. (See notes.)

**Reagents: Standard Ferrous Solution.** — Ferrous ammonium sulphate N/10 solution, contains 39.214 grams per liter. It is advisable to take 40 grams per 1000 cc. Clear the solution with a few drops of strong $H_2SO_4$.

Molecular weight of $FeSO_4.(NH_4)_2SO_4.6H_2O = 392.14$.

**Standard Potassium Dichromate.** — $K_2Cr_2O_7$, mol. wt. 294.2. Since the salt used as an oxidizing agent has three available oxygens per molecule, one-sixth of its molecular weight, i.e. 4.903 grams of the pure salt per 1000 cc. are required for a N/10 solution.

**Standard Potassium Permanganate.** — $KMnO_4$, mol. wt. 158.03. Since the salt used as an oxidizing agent has five available oxygens per two molecules $2\ KMnO_4 = K_2O.Mn_2O_2.5O$, or $2\frac{1}{2}$ O per molecule, equivalent to 5 H, therefore a normal solution contains 1/5 of the gram molecular weight, i.e. 31.606 grams per 1000 cc. For a N/10 solution 3.2 grams of the pure salt are dissolved in water and made up to 1000 cc. The reagent after standing several days is standardized against pure iron, or sodium oxalate. Details of this preparation are given in the chapter on reagents.

**Procedure.** — 1. *Solution.* — Half to one gram of ore or 1 gram of chrome steel are dissolved according to directions given under Preparation and Solution of the Sample, the ore preferably by peroxide fusion and the steel by solution with sulphuric acid (1 : 3) with subsequent treatment with nitric acid and potassium permanganate as stated. The solution should be free from nitric acid or potassium permanganate. The removal of iron is not necessary as is the case with the potassium iodide method. The solution having been obtained, proceed as follows :

2. *Reduction.* — The solution should contain not over 0.17 gram of chromium if N/10 reagents are to be used. If oxidizing agents are suspected, boil the solution, having added sufficient sulphuric acid to almost neutralize any alkaline salts present. The preliminary treatment for obtaining the solution should have been sufficient so that this procedure should not be necessary here. Now acidify the solution with $H_2SO_4$, adding 5 cc. excess.

3. To the cooled solution add N/10 ferrous ammonium sulphate, until the solution changes from the yellow color to olive green and finally grass green. For every 0.1 gram of chromium present about 65 cc. of the reagent will be required.

4. Allow to stand for about five minutes. Now titrate the excess of the ferrous salt with standard permanganate or dichromate.

*Potassium Permanganate Titration.* — This reagent is generally preferred, but the solution should be free from hydrochloric acid. (Notes.)

5. Add the oxidizing reagent until the green color gives place to a tinge of violet. At the end point the solution appears to darken. A slight excess of permanganate gives the solution a pinkish color, readily distinguished in the green. A little practice enables one to get this with great accuracy. Addition of 3–5 cc. of syrupy phosphoric acid gives a sharper end point, as it fades the color due to iron. The color of the permanganate should hold for one minute.

6. The permanganate titrates the excess of ferrous salt present. Convert the cc. of N/10 ferrous solution to exactly N/10 by multiplying by the normality factor, if this is necessary. Also convert the cc. of permanganate required to exact cc. of N/10 if the reagent is not exactly N/10. We have now the exact cc. of N/10 strength that were added to reduce the chromate, and the cc. of N/10 permanganate required to oxidize the excess of the ferrous solution. The difference is the cc. of N/10 ferrous sulphate that were used by the chromate in its reduction to $Cr_2O_3$, of which each cc. required is equivalent to 0.001733 g. Cr.

(cc. N/10 Fe solution − cc. N/10 $KMnO_4$ solution) × 0.001733 = g. Cr.

*Potassium Dichromate Titration.* — This reagent may be used if free hydrochloric acid is present in the reduced chromate solution.

5ª. Add the dichromate reagent to the reduced chromate solution until a drop of the sample placed on a white glazed surface with a drop of potassium ferricyanide reagent no longer gives a blue color.

6ª. Convert the cc. of dichromate required to exactly N/10 equivalent, if the reagent is not exactly N/10 in strength. (Multiply by the normality factor.)

Subtract the cc. of N/10 dichromate from the cc. of N/10 ferrous salt used and multiply the difference by 0.001733 = gram Cr.

Notes. As seen by the reaction, two molecules of chromium lose three atoms of oxygen, equivalent to six atoms of hydrogen, hence Cr = 3H and a normal solution would contain $\frac{1}{3}$ the atomic weight of Cr = 17.33 grams per liter.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Determination of Chromium in a Soluble Chromate

To a concentrated solution of potassium iodide is added a known amount of the soluble chromate dissolved in a little water. The liberated iodine is now titrated with standard thiosulphate reagent.

$$N/10\ Na_2S_2O_3 = 0.001733\ g.\ Cr.$$

### Determination of Chromium in Chromite

About 0.2 g. of the powdered ore is fused with ten times its weight of $Na_2O_2$ in a porcelain crucible, placed inside a larger crucible. The melt is dissolved in water and the $Fe(OH)_3$ filtered off. The filtrate is evaporated to dryness, the residue taken up with as little water as possible and about two grams of KI added. The solution is now diluted to about 300 cc. and the liberated iodine titrated with standard thiosulphate.

$$N/10\ Na_2S_2O_3 = 0.001733\ g.\ Cr.$$

### Rapid Method for Determination of Chromium in Steel

Three grams of steel are dissolved in 100 cc. of sulphuric acid 1 to 4. If it does not dissolve rapidly a crystal of $(NH_4)_2(SO_4)_2$ will hasten it. After solution add conc. $HNO_3$ until iron is oxidized. Boil for one minute, add 10 cc. 5% $AgNO_3$, remove from flame and add crystals of Am. Persulphate until all the chromium is oxidized as shown by the manganese being converted to Permanganate. Boil until persulphate is broken up and then add 5% sodium chloride until permanganate is destroyed as shown by the disappearance of the red color. An excess of salt solution should be avoided. Cool thoroughly and titrate with ferrous sulphate, determining the excess with permanganate. These solutions are standardized on a known sample of chrome steel.

Two determinations run simultaneously will check within 0.2%.

### Colorimetric Estimation of Small Amounts of Chromium with Diphenyl Carbazide

Diphenyl carbazide, $CO(MH.NH.C_6H_5)_2$, gives a violet color with chromic salts or chromates in acid solution, the intensity of the color being proportional to the concentration of the chromate. Less than 0.0001 milligram of chromium may be detected by this reagent. The following procedure may be used for determining traces of the element:

1 to 2 grams of the substance, which has been brought into solution with water or acid, is treated with an excess of sodium peroxide to oxidize chromium, and the solution filtered. The filtrate, concen-

trated to 75–80 cc. is acidified with hydrochloric, so that there is present about 5 cc. of free concentrated acid (sp. gr. 1.19) per 100 cc. of Solution. The Solution transferred to a Nessler tube, is treated with 1 cc. of the reagent, and the color compared with standards containing the same reagents as the sample examined. A colorimeter may be used and comparison made with a standard according to details given for the colorimetric comparison of traces of lead or titanium.

**Preparation of Diphenyl Carbazide Reagent.** — One tenth of a gram of the compound is dissolved in 10 cc. of glacial acetic acid and diluted to 100 cc. with ethyl alcohol.

Diphenyl carbazide may be made by heating a mixture of 15 grams of urea with 50 grams of phenyl hydrazine four hours, finishing at 155° C. The solid product is crystallized three times with alcohol. A light straw-colored product is obtained. A white product is obtained if the urea is cut down to 5 grams, the yield, however, is only 25 per cent of that obtained by the first method and the compound possesses no advantages.

## COBALT

**Co, at.wt. 58.97; sp.gr. 8.7918; m.p. 1478° C.; b.p. unknown; oxides, $Co_3O_4$, $Co_2O_3$, CoO, $CoO_2$**

The analysis of cobalt is generally required in the valuation of ores of cobalt and nickel, which are generally arsenides, arsenates, sulphides, oxides, carbonates and silicates. It is determined in mattes, speiss, blister copper, smalts,[1] slags, catalytic agents, vat liquors, alloys of iron, copper, nickel and other metals.

### OCCURRENCE

Cobalt is found native in meteoric iron. It occurs in a number of minerals, frequently associated with nickel, iron, arsenic, antimony, sulphur.

**Minerals.** — *Linnaeite*, Cobalt pyrites, $(CoNi)_3S_4$, a steel gray opaque, brittle mineral with metallic lustre, often with reddish tarnish, black streak; hardness 5.5. Soluble in nitric acid to red solution. Borax bead gives a blue color.

*Smaltite*, $(Co.Ni)As_2$, tin white to steel gray, brittle, opaque mineral with metallic lustre, usually occurs granular massive, occasionally in isometric crystals: cleavage ocathedral; hardness 5.5–6.

*Cobaltite*, Cobalt Glance, CoAsS, resembles linnaeite in massive state. Silver white to gray, opaque, metallic mineral with black streak, brittle with cubic cleavage; hardness 5.5. Erythrite, $Co_3(AsO_4)_2.8H_2O$.

Cobalt is usually estimated as metal; either reduced by hydrogen from the ignited oxide or reduced by electrolysis from an ammoniacal solution of its salts. Sometimes, however, it is estimated as oxide; usually as $Co_3O_4$. The reduction of the oxide by hydrogen may be carried out in conjunction with any process giving an oxide, hydroxide, carbonate, nitrate, chloride or an organic compound, as a final product.

The reduction of the metal, in solution, by electrolysis, must be accomplished in a strongly ammoniacal solution free from copper and nickel, as these metals are deposited with the cobalt on the cathode. When desirable the copper and nickel may be estimated after the electrolysis by dissolving the deposit from the cathode and proceeding in the usual manner.

Cobalt has remarkable catalytic properties in the oxidation of ammonia to nitric acid. This property is accentuated by the presence of certain other elements, such as bismuth, beryllium (Glucinum) cerium, aluminum, etc., present in very small proportion, the efficiency being equal to that obtained with platinum.

[1] Smalts, blue pigment of cobalt glass, finely ground.

### DETECTION

See method of solution given on following page.

After the removal of the elements precipitated by hydrogen sulphide from acid solution, a little nitric acid is added to the solution to oxidize to the ferric state any ferrous salts which may be present, and ammonia is added until its odor is distinctly perceptible, to precipitate iron, aluminum and chromium. This precipitate is removed by filtration and hydrogen sulphide passed through the ammoniacal solution to precipitate cobalt, nickel, manganese and zinc. After collecting this precipitate it is washed thoroughly with cold hydrochloric acid of approximately 1.035 specific gravity, to remove manganese and zinc. A small quantity of the residue is fused with borax in the loop of a platinum wire. A blue color in the cold bead indicates cobalt. This test is masked in the presence of large quantities of nickel. In this case the residue is dissolved in hydrochloric acid to which a few drops of nitric acid have been added and the solution evaporated to dryness. The residue is redissolved in water, acidified with hydrochloric acid and the cobalt precipitated with a hot solution of nitroso-beta-naphthol in 50% acetic acid. A brick red precipitate indicates cobalt.

**Potassium sulphocyanate,** KCNS, produces a blue color with cobalt. Alcohol and ether are added to this solution and shaken. The ether layer is colored blue by cobalt. If iron is present a solution of sodium thio-sulphate, $Na_2S_2O_3$, is added until the red color disappears, the solution filtered and then treated with the alcohol-ether mixture.

**Potassium Nitrite,** $KNO_2$, added to a neutral or slightly acid solution containing acetic acid, will precipitate cobalt as a yellow complex nitrite having the formula $K_6Co_2(NO_2)_{12}$.

A solution of *dicyandiamidine sulphate* and sodium hydroxide added to a cobalt solution to which ammonia has been added until the odor is distinctly discernible, and containing from 10 to 20 cc. of 10% sugar solution, will change the color of the solution to red or reddish violet. If large quantities of nickel are present the color will be yellow or reddish yellow, after which the nickel will separate out in brilliant crystals, leaving the cobalt in solution, coloring it as described above.

A concentrated solution of *ammonium sulphocyanate* added to a cobaltous solution colors it blue. On dilution this becomes pink. Amyl alcohol or a mixture of amyl alcohol and ether 1 : 1, added to this and shaken, extracts this blue compound. Iron sulphocyanate, $Fe(CNS)_3$, likewise colors the ether-alcohol extract red, which may mask the cobalt blue. By addition of sodium carbonate solution ferric hydroxide precipitates, while the cobalt color will remain after this treatment.

## GRAVIMETRIC METHODS FOR THE DETERMINATION OF COBALT

### Preparation and Solution of the Sample

**General Procedure for Ores.** — The ores containing cobalt vary so widely in their chemical nature that it is difficult to lay down a method for treating all ores. However, as the principal ores contain the cobalt as a sulphide or arsenide the same general methods may be used in the majority of cases. In all cases it is necessary to prepare the sample for treatment by grinding finely. Usually either of the above ores may be brought into solution by heating with strong nitric acid or a mixture of nitric and hydrochloric acids, except silver-bearing ores, which may usually be dissolved in a mixture of nitric and sulphuric acids.

While it is desirable to use no more acid than is necessary to bring the sample into solution, an excess will not interfere, as it may be driven off by evaporation and in the event of determining the cobalt electrolytically it is essential that the solution be free from nitric acid, so that this evaporation becomes part of the procedure.

In the case of especially refractory ores or oxides of cobalt or nickel, a fusion with potassium bisulphate will usually be found sufficient as a preliminary treatment to enable it to be brought into solution.

**Metallic Cobalt, Nickel and Cobalt Alloys.** — Metallic cobalt dissolves readily in nitric acid, as do nickel and the ordinary cobalt alloys. There are some alloys of cobalt, however, which require fusion with sodium peroxide before they become amenable to further treatment. Among these are certain cobalt-chromium alloys.

**Separation of the Ammonium Sulphide Group Containing Cobalt from the Hydrogen Sulphide Group.** — Mercury, Lead, Bismuth, Copper, Cadmium, Arsenic, Antimony, Tin, Gold, Molybdenum, etc.

Hydrogen sulphide passed into a hydrochloric acid solution containing from 5 to 7 cc. of concentrated hydrochloric acid per 100 cc. of solution, precipitates only the members of that group and silver, whereas the members of the subsequent groups remain in solution. If the solution is too acid, lead and cadmium are not completely precipitated.

**Separation of the Ammonium Sulphide Group from the Alkaline Earths and Alkalies.** — Ammonium sulphide, free from carbonate, added to a neutral solution containing the above elements in the presence of ammonium chloride, precipitates only the members of this group; the alkaline earths, metals, magnesium and the alkalies remain in solution. A second precipitation should be made if large quantities of the alkaline earths or alkalies are present.

**Separation of Cobalt and Nickel from Manganese.** — The solution of the chlorides or sulphates of cobalt or nickel is treated with an excess of sodium carbonate and then made strongly acid with acetic acid. About 5 grams of sodium acetate for each gram of cobalt or nickel present is now added, the solution diluted to 200 cc. and heated to about 80° C. and saturated with hydrogen sulphide. Cobalt and nickel are precipitated as sulphides and the manganese remains in solution. The filtrate is concentrated, and colorless ammonium sulphide added when the cobalt and nickel that may have passed into solution from the hydrogen sulphide treatment will be precipitated. The treatment should be repeated with the second filtrate to ensure complete precipitation of the cobalt and nickel.

### PRECIPITATION OF COBALT BY NITROSO-BETA-NAPHTHOL

Nitroso-beta-naphthol, $C_{10}H_6(NOH)$, added to a hydrochloric acid solution of cobalt, precipitates cobalti-nitroso-beta-naphthol, $Co(C_{10}H_6O(NO))_3$; nickel, if present, remains, in solution. The method is especially suitable for the determination of small amounts of cobalt in the presence of comparatively large amounts of nickel. The cobalt precipitate is voluminous, so that the sample taken for the determination should not contain over 0.1 gram of cobalt. The reagent will also precipitate copper and iron completely from solution, and silver, bismuth, chromium and tin partially; but mercury, lead, cadmium, arsenic, antimony, aluminum, manganese, nickel, glucinum, calcium and magnesium remain in solution.

**Procedure.**— To the solution containing the cobalt is added a freshly prepared hot solution of nitroso-beta-naphthol, in 50% acetic acid, as long as a precipitate is produced. After allowing it to settle, more of the reagent is added to insure complete precipitation of the cobalt. The compound is allowed to settle for two or three hours, the clear solution decanted through a filter and the precipitate washed by decantation with cold water, then with warm 12% hydrochloric acid solution to remove the nickel, and finally with hot water until free of acid.

The brick-red precipitate is dried, then ignited in a weighed platinum crucible (Rose crucible), first over a low flame and finally at a white heat, the crucible being covered by a platinum cover (Rose crucible type) with a platinum tube, through which is passed a slow current of oxygen. The residue is weighed as $Co_3O_4$. The oxide may be reduced in a current of hydrogen and weighed as metallic cobalt. Ignited in the presence of $CO_2$ the oxide CoO is formed.

### PRECIPITATION OF COBALT BY ELECTROLYSIS

Metallic cobalt is readily deposited from an ammoniacal solution of the sulphate, but in the presence of copper and nickel these are also completely precipitated on the cathode; so, in case it is desired to determine the cobalt alone it is necessary to separate these metals from the solution before electrolysis or to determine them separately after electrolysis in a solution of the metallic deposit. In practice the copper is usually separated before electrolysis and the nickel, if determined separately, is estimated afterward by one of the methods given under Nickel, the cathode deposit being dissolved for this purpose.

**Procedure.**— After preparation and solution of the sample the usual separations with hydrogen sulphide in acid solution are made if necessary. In most cases it is necessary to pass hydrogen sulphide through the warmed solution for at least one hour to insure the complete precipitation of arsenic. Filter and boil to expel hydrogen sulphide. Add 5 cc. of hydrogen peroxide to insure oxidation of iron compounds to ferric state and add ammonium hydroxide until slightly alkaline to litmus. Filter off ferric hydroxide and wash with water

containing a small quantity of ammonium hydroxide. Redissolve and reprecipitate this ferric hydroxide in the above manner, using a little hydrogen peroxide in each instance, until the last traces of cobalt have been removed from it, keeping the filtrates, which should be as small as possible, to add to the main filtrate. If much iron is present this is best removed as the basic acetate.

**Electrolysis.** — If the treatment of the iron precipitate has made a large volume of solution this may be reduced by evaporation, after which 50 cc. of strong ammonia are added and the solution electrolyzed, using direct current of 2 volts and 0.5 ampere per square decimeter. The electrodes should be platinum, the anode a spiral wire and the cathode either a hollow cylinder or a cylindrical gauze. By agitating the solution, raising the voltage and the current density, the rate of deposition may be increased. In a properly agitated solution the deposition may be completed in forty-five minutes.

The current should not be cut off until the solution is tested to determine if the electrolysis is complete. This is done by mixing a drop or two of the solution from the end of a stirring rod with a few drops of ammonium sulphide. If the electrolysis is complete the mixture will remain colorless, but if some cobalt still remains in the solution the mixture will be darkened. After the electrolysis is complete the cathode is carefully removed from the solution and dipped into a beaker of clean water, after which it is washed with alcohol, preferably ethyl alcohol.

If a large number of electrolytic determinations are to be made, it is convenient to have a wide-mouthed bottle with a well-ground-in glass stopper or a cork stopper for holding the alcohol for the preliminary washing. The mouth should be large enough to receive the cathode without pouring out the alcohol. The cathode may be lowered into the alcohol in this bottle, which should only be partly filled, and then rinsed again by pouring fresh alcohol over it and allowing it to drain into the wide-mouth bottle. This allows a great many cathodes to be washed with a comparatively small quantity of alcohol. Directly after the final washing with alcohol the cathode is passed through the flame of a Bunsen burner and the alcohol ignited. After this is entirely burned off the cathode is placed in a desiccator to cool and when cool is weighed. The increase in weight of the cathode is the weight of cobalt in the sample if the solution had been free from nickel before electrolysis. If the nickel remained in the solution the increase in weight of the cathode represents the cobalt and nickel in the sample. If it is desired to determine the cobalt and nickel together the increase in weight of the cathode is divided by the weight of the sample and multiplied by 100 to obtain the percentage. If it is desired to obtain the percentage of cobalt separately, the plate is dissolved from the cathode in a few cc. of nitric acid and the nickel determined in the resulting solution by precipitation with dimethylglyoxime after which the cobalt is found by difference.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Cobalt in Metallic Cobalt and Ferro-cobalt

Cobalt is usually determined in metallic cobalt and ferro-cobalt by electrolysis, after separation of the elements precipitated by hydrogen sulphide in acid solution and elimination of iron, if present in large quantities. In case it is desired to estimate nickel separately it is precipitated by dimethylglyoxime as described in the chapter on Nickel, before electrolysis, taking the solution down to sulphur trioxide fumes, diluting with water and adding ammonium hydroxide in excess and electrolyzing. In case the solution is electrolyzed before separating the nickel the determination of this element may be made in the solution of the electrolytic deposit dissolved in acid, the cobalt then found by difference.

**Procedure.**— Dissolve 1 gram of well-mixed drillings in the least possible quantity of nitric acid and add 20 cc. of 1 : 1 sulphuric acid. Evaporate to fumes of sulphur trioxide and allow to fume strongly for ten minutes. This insures the complete elimination of nitrates, which would interfere subsequently with the electrolysis. Cool and dilute carefully with 20 cc. of water. Heat the solution to nearly boiling and pass in hydrogen sulphide for one hour to precipitate copper and arsenic. Filter and boil the solution to expel the last traces of hydrogen sulphide. Add 2 cc. of hydrogen peroxide to oxidize ferrous compounds to ferric state, and add ammonium hydroxide until slightly alkaline to litmus paper and heat to boiling. Filter off the ferric hydroxide and wash with water containing a small quantity of ammonium hydroxide. Redissolve the precipitate in a little 1 : 1 sulphuric acid, adding a little hydrogen peroxide to keep the iron in the ferric state, and reprecipitate in the same manner as that described above. In presence of comparatively large amounts of iron the basic acetate separation of iron is necessary, as $Fe(OH)_3$ occludes cobalt and nickel. The filtrates from these precipitations are added to the main one.

In determining the cobalt in metallic cobalt it is not necessary to filter off the iron precipitate, if this is small, as it has been found by W. L. Rigg, of Deloro, Ontario, that this precipitate does not interfere with the accuracy of the determination. The iron content may be up to 5% without interfering seriously with the electrolysis.

The solution is made ammoniacal with 50 cc. of strong ammonium hydroxide and electrolyzed as described above.

### Cobalt in Steel

This determination is a modification of the nitroso-beta-naphthol method already described, as worked out in the laboratory of the Firth Stirling Steel Company, McKeesport, Pa. The procedure as described by Mr. Giles, Chief Chemist, is as follows.

Two grams of the sample are weighed into a 500 cc. Erlenmeyer flask and dissolved in 50 cc. of concentrated hydrochloric acid. When the sample is completely decomposed 10 cc. of concentrated nitric acid are added to oxidize the iron, tungsten, etc. The solution is evaporated to 10 cc.; 50 cc. of water are added; the contents of the flask are then transferred to a 500 cc. volumetric flask and cooled to room temperature. A fresh solution of zinc oxide is added in slight excess, the contents of the flask diluted to the mark, well mixed, transferred back to the original Erlenmeyer flask and allowed to settle. Filter 250 cc. (equivalent to 1 gram of the sample) through a dry filter paper, transfer it to a 500 cc. flask, then add 6 cc. of concentrated hydrochloric acid.

The solution, which should now be between 300 and 350 cc. in volume, is heated to boiling and 10 cc. of freshly prepared solution of nitroso-beta-naphthol (1 gram of salt to 10 cc. of glacial acetic acid) are added for each 0.025 gram of cobalt present. Continue to heat for two minutes, remove from hot plate, shake well, and set aside until the bright red precipitate settles, which will only take a few minutes. Filter the hot solution and wash the flask out with hot 1 : 1 hydrochloric acid and then wash the flask out with hot acid of the same strength. Wash the paper alternately with hot (1 : 1) hydrochloric acid and hot water until it has been washed five times with the acid, then wash ten times with hot water. The precipitate is transferred to a quartz or porcelain crucible, heated gently to expel the carbonaceous matter, then at a high temperature until ignition is complete. After cooling the crucible is weighed and the weight of the residue ($Co_3O_4$) is multiplied by 0.734 to obtain the percentage of cobalt weighed as metal.

### Cobalt in Ores and Enamels [1]

The determination of cobalt in ores and enamels is usually made by a slight variation of the above methods. The silica is separated in the usual manner by taking down to dryness with hydrochloric acid and the warmed solution is treated with hydrogen sulphide to precipitate sulphides insoluble in acid solution. Aluminum, chromium and iron are precipitated by adding ammonium hydroxide to the oxidized solution. In the enamel industry it has been the practice to follow R. W. Landrum's method, in which the cobalt, manganese and nickel are precipitated together as sulphides and filtered off. The manganese is dissolved from this precipitate with cold hydrogen sulphide water acidified with one-fifth its volume of hydrochloric acid (sp.gr. 1.11). The residue of cobalt sulphide is burned in a porcelain crucible, dissolved in aqua regia and evaporated with hydrochloric acid. The platinum and copper, if they are present, are thrown down by passing hydrogen sulphide through the solution. The filtrate is made ammoniacal and the cobalt is precipitated with hydrogen sulphide. This is filtered off and washed with water containing a small quantity of ammonium sulphide. The precipitate is either ignited and weighed as oxide or reduced in hydrogen to metallic cobalt, taking care to cool it thoroughly in an atmosphere of hydrogen before allowing it to come into contact with the atmosphere of the room, as finely divided cobalt is decidedly pyrophoric and oxidizes readily, particularly if reduced at a low temperature.

Instead of igniting the sulphide precipitate it may be dissolved in hot 1 : 1 sulphuric acid solution with the aid of a little nitric acid and treated as described under Precipitation of Cobalt by Electrolysis.[2]

[1] R. W. Landrum, Trans. Am. Cer. Soc., 12, 1910.

[2] The greater portion of this chapter was contributed by W. L. Savell.

## COPPER

**Cu, at.wt. 63.57; sp.gr. 8.89$^{20°}$; m.p. 1083° (in air 1065° C.); b.p. 2310°; oxides $Cu_2O$ and CuO**

The estimation of copper is required in the following substances: *In ores*[1] *of copper*, in which it occurs as native copper or combined as sulphide, oxide, carbonate, chloride, silicate and basic sulphate; in furnace slags, mattes, concentrates, blister copper, bottoms. The determination of copper is required in the analysis of alloys containing copper, brass, bronze, etc. It is occasionally looked for as an undesirable impurity in food products. It is determined in salts of copper, in insecticides, germicides, etc.

### OCCURRENCE

Copper is found native in large quantities; it occurs combined in a large number of minerals; traces are found in animals and plants. Among the more important minerals are the following:

**Minerals.** — *Native Copper*, Cu. A red, soft, malleable metal; opaque; copper red-streak; usually in sheets, or masses varying from small grains to hundreds of tons in weight. The metal tarnishes almost black. In blow pipe test the metal fuses to a globule. In beads O.F. green when hot, blue when cold; R.F. opaque red. Easily soluble in nitric acid giving green solution. Addition of metallic iron or zinc, etc. (see Electromotive Series) will precipitate metallic copper from its solution. Ammonia precipitates a blue compound, soluble in excess forming a deep blue solution.

*Chalcocite*, Copper Glance, $Cu_2S$, a brittle, opaque, grayish black, granular or compact mineral, often coated with malachite (green), lead gray streak; hardness 2.5–3.

*Bornite*, Purple Copper Ore, Horse Flesh Ore, $Cu_5FeS_4$, a dark copper-red, brownish or violet blue mineral with metallic lustre; opaque; brittle; grayish-black streak; hardness 3.

*Chalcopyrite*, Copper Pyrites, Yellow Copper Ore, $CuFeS_2$, a bright brass-yellow mineral with metallic lustre; opaque; brittle; greenish-black streak; usually massive but sometimes in crystals; hardness 3.5–4.

[1] Other Minerals of copper: Covellite, CuS; Tennantite, $4Cu_2S.As_2S_3$; Enargite, $3Cu_2SAs_2S_3$; Stannite, $Cu_2S.FeS.SnS_2$; Atacamite, $CuCl_2.3Cu(OH)_2$; Chrysocolla, $CuSiO_3.2H_2O$; Turquois, $CuO.3Al_2O_3.2P_2O_5.9H_2O$; Brochantite, $CuSO_4.3Cu(OH)_2$; Linarite, (Pb, Cu) $SO_4$.(Pb, Cu) $(OH)_2$; Chalcanthite, $CuSO_4.5H_2O$.

*Tetrahedrite*, Gray Copper Ore, $Cu_8Sb_2S_7$, a fine grained, brittle, opaque, steel to dark gray or black mineral with metallic lustre; reddish-brown to black streak; hardness 3–4.5.

*Cuprite*, Red Oxide of Copper, Ruby Copper Ore, $Cu_2O$, crimson, scarlet, vermillion or brownish-red, transparent to opaque, brittle mineral with adamantine to dull lustre; fine grained masses, transparent, isometric crystals, octahedrons or cubes; brownish red streak; hardness 3.5–4.

*Malachite*, Green Carbonate of Copper, $CuCO_3.Cu(OH)_2$, bright green masses, silky fibrous structure, sometimes stalactitic, or in dull-green earthy masses; translucent to opaque; brittle; pale-green streak; hardness 3.5–4.

*Azurite*, Blue Carbonate of Copper, $2CuCO_3.Cu(OH)_2$, a dark blue, brittle, translucent to opaque mineral with vitreous lustre; frequently occurs incrusting other copper minerals; blue streak; hardness 3.5–4.

## DETECTION

Copper is precipitated in an acid solution by $H_2S$ gas, along with the other members of the hydrogen sulphide group. The insolubility of its sulphide in sodium sulphide is a means of separating copper from arsenic, antimony, and tin. The sulphide dissolves in nitric acid (separation from mercury) along with lead, bismuth, and cadmium. Lead is precipitated as $PbSO_4$ by sulphuric acid and bismuth as the hydroxide, $Bi(OH)_3$, upon adding ammonium hydroxide. Copper passes into the filtrate, coloring this solution blue,

$$Cu(OH)_2.2NH_4OH.(NH_4)_2SO_4.$$

**Flame Test.** — Substances containing copper (sulphides oxidized by roasting), when moistened with hydrochloric acid and heated on a platinum wire in the flame, give a blue color in the reducing flame and a green tinge to the oxidizing flame.

**Wet Tests.** — Nitric acid dissolves the metal or the oxides (sulphides should be roasted), forming a green or bluish-green solution. Ammonium hydroxide added to this solution will precipitate a pale blue compound, which dissolves in excess with the formation of a blue solution. (Nickel also gives a blue color.)

**Hydrogen sulphide** passed into a copper solution which is free of $SO_2$ or an oxidizing agent, but somewhat acid with a mineral acid, precipitates at once brownish black CuS or $Cu_2S$ (distinction from nickel, cobalt and zinc), which is difficultly soluble in strong, hot HCl (distinction from antimony), insoluble in fixed alkaline polysulphides (distinction from gold and platinum), soluble in alkaline cyanides (distinction from lead, bismuth, cadmium, mercury and silver), soluble in nitric acid (distinction from sulphide of mercury),

with production of a bluish solution (distinction from all other metals except silver).

**Potassium ferrocyanide** precipitates from an acid or neutral solution of a cupric salt reddish-brown cupric ferrocyanide, which can be confused only with similarly colored precipitates from molybdenum or uranium solution.

**Cupric salts** in halogen acid solution are reduced to colorless cuprous compounds by metallic copper, stannous chloride and sulphurous acid; and in alkaline solution are reduced by grape sugar, arsenious or sulphurous acids.

**Metallic iron or zinc** added to an acid solution containing copper precipitates the red metal; if this precipitate is dissolved in nitric acid, brownish red fumes are evolved (nitrous oxides). To the nitric acid solution an *excess of ammonium hydroxide* is added, the greenish solution will change to *a deep blue* if copper is present.

## SUGGESTIONS FOR THE STUDENT

Read the preliminary statements as to methods of solution and separations. For the gravimetric determination of copper use the rapid electrolytic method described on page 245; for a volumetric determination of copper follow the directions under the Potassium Iodide method on page 253.

## METHODS FOR DETERMINATION OF COPPER

### Preparation and Solution of the Sample

Nitric acid is the most active solvent. Hydrochloric and sulphuric acids are effective in dissolving metallic copper only in presence of an oxidizing agent. The oxides of copper may be dissolved in hydrochloric or sulphuric acid, but nitric acid is commonly used. Some refractory furnace products are most easily decomposed by treatment with hydrofluoric and fuming sulphuric acid followed by a bisulphate fusion.

**Ores.** — If the ore consists practically of a single mineral, the fineness of the sample need not exceed 80 mesh. If the ore is a mixture of minerals, lean and rich in copper, the laboratory sample should pass a 120-mesh sieve.

Metallic particles or masses are separated at some stage in the process of sampling and made into a separate sample. If the metallic portion is a small percentage of the total sample and consists of particles, the copper value of which is known to vary by a few per cent, no attempt is made to refine the sample of such, but a large portion, 10–100 grams, is taken for analysis and the copper determined in an aliquot part of the solution.

**Sulphide and oxidized Ores and Matte.** — One to five grams of the sample are dissolved by adding 10–20 cc. of dilute nitric acid (1.2 sp.gr.), or 10 cc. of strong nitric acid saturated with potassium chlorate, and allowing the mixture to stand in a warm place for about 15 minutes before applying heat. Decomposition is completed by evaporating to small volume in a casserole and continuing to dryness after addition of 10 cc.of hydrochloric acid, or by adding 5–10 cc. of 50% sulphuric acid, to the assay in a flask or tall beaker and heating to fumes. The residue is taken up by warming with 20 cc. of 10% $H_2SO_4$, diluting, boiling and filtering the residue of silica, lead sulphate and silver chloride from the copper solution. Copper passes into solution.

**Metals.** — A casting of a copper alloy and even of refined copper is not homogeneous, and the zones of segregation of the constituents of the alloy (usually roughly parallel to the cooling surfaces) are the more sharply defined as the conditions which favor diffusion of the eutectic prevail, therefore, unless the casting be quite thin and quickly cooled, a satisfactorily representative sample of it cannot be obtained from a single drill hole. A single casting may be sampled by complete cross-sectional cuts by a suitable saw or by a series of drill holes located in such a manner as to amount substantially to one or more cross-sectional cuts. Steel is usually present as a contaminant of the drill or saw shavings from refined copper and the tougher alloys and should be removed by a magnet. The metal may now be brought into solution by treatment with nitric acid.

## METHODS OF ISOLATING COPPER

**Separation of Copper as Cuprous Thiocyanate.** — Isolation of copper from solutions containing iron, nickel, cobalt, zinc, cadmium, arsenic, antimony and tin may be accomplished by this method. When much arsenic is present, precipitation should be from a solution in which hydrochloric is the only free strong acid. Unless previously removed from the solution, lead, mercury, tellurium and the precious metals will contaminate the precipitate. Selenium may be a contaminant when present in considerable quantity, sometimes when the only free acid is sulphuric, always when hydrochloric acid is present.

Cuprous thiocyanate, besides being the medium of separation of copper from interfering elements preliminary to its determination by the standard electrolytic, iodide or cyanide methods, is the basis of a number of other more or less useful gravimetric and volumetric methods of determining copper. The details of the procedure of procuring the precipitate vary to some extent with its object. Low grade copper ores may be conveniently determined by this method.[1]

**Procedure.** — To the cold, concentrated and very slightly acid copper solution (which must be free of any oxidizing agent) sulphur dioxide, gaseous or in solution, or a solution of an alkaline bisulphite or metabisulphite is added somewhat in excess of the quantity theoretically required to reduce all the copper and ferric iron present.

The liquid is cooled if hot, and then, with constant stirring, a solution of alkali thiocyanate of about normal strength is added until precipitation ceases. Reaction: $2CuSO_4 + 2KCNS + H_2SO_3 + H_2O = 2CuCNS + 2H_2SO_4 + K_2SO_4$. It is common practice to continue introduction of $SO_2$ throughout precipitation. The precipitate is allowed to stand until it is white and the liquid above it is clear. The presence of $FeSO_4$ accelerates conversion of cupric to cuprous thiocyanate when sulphuric is the only free acid. The precipitate is filtered off with the aid of reduced pressure through doubled filter papers of tight texture and washed with cold water until a washing is obtained which gives but very slight indication of thiocyanate when tested with a ferric salt.

The precipitate is inclined to float and creep with the capillary film of fluid, so precautions must be taken in its manipulation to avoid loss of copper on account of this characteristic.

The collected precipitate may now be treated in several ways which will produce a solution fit for the determination of copper by one of the standard methods. (*a*) The filter and precipitate are transferred to a porcelain or silica crucible which is very much larger than the volume of the wet precipitate, dried slowly in an oven or

[1] With high grade ores or copper bullion a trace of copper (usually less than 0.0005 g. Cu) will pass into the filtrate when the copper precipitated amounts to 0.5 grams Cu. The loss with low grade copper ores is negligible.

muffle and finally incinerated. Some operators made the final washing with 20% alcohol to facilitate drying or with a weak solution of an alkali nitrate to aid incineration. The residue is dissolved in the crucible with hot, strong nitric acid. (*b*) The point of the filter is punctured and the precipitate washed with as little water as possible into a flask or tall beaker. The filter is finally cleansed of adherent precipitate by washing with dilute nitric acid. The filter is dried, incinerated and dissolved separately or added to the main precipitate before its decomposition. 15 cc. strong nitric acid is added for each gram or fraction of a gram of copper present and the covered beaker or funnel-closed flask, allowed to stand in a warm place until the precipitate is dissolved, then boil until solution is free of the nitrogen gases. It is the practice of some to add now 10–15 cc. of sulphuric acid and evaporate to fumes. Because evolution of gas during dissolution of the precipitate is profuse, care must be taken to expel the gas slowly to prevent boiling over.

**Separation of Copper by Precipitation in Metallic Form by a More Positive Element.** — Metallic aluminum or zinc is more commonly used in this procedure. A strip of pure aluminum or zinc, placed in the neutral or slightly acid solution, causes the complete deposition of copper. To obtain quick precipitation, a sheet of aluminum, 2.5 by 14 cm., is bent to raise the metal from the bottom of the beaker, placed in a covered 150 cc. beaker containing the copper solution, which should be not much over 75 cc. in volume and should hold about 10% of free $H_2SO_4$. Boil 7–10 minutes. The copper is removed mechanically from the displacing metal and dissolved in nitric acid and then estimated.

A method of precipitation by means of powdered aluminum is recommended especially for separation of copper from large amounts of iron, iron ores and iron ore briquettes. The solution of the bisulphate fusion of the iron ore is heated until bubbles appear over the bottom of the containing beaker. Aluminum powder is now added in small portions at a time, in sufficient quantity to reduce the iron, the solution becoming colorless. The solution is now heated until the aluminum completely dissolves. Metallic copper is precipitated. It is advisable to add 25 cc. of water saturated with $H_2S$ gas to precipitate traces of copper in solution. The solution is filtered while hot through a close thick filter, and washed six times, keeping the residue covered with water to prevent oxidation by air. The copper is now dissolved in hot dilute nitric acid, evaporated to small volume and determined by the procedure preferred. The potassium iodide method gives excellent results.

Occasionally the aluminum lies inert in the solution. If this occurs two or three drops of hydrochloric acid (do not use much) will start a vigorous action and cause a rapid precipitation of metallic copper.

## DEPOSITION OF METALLIC COPPER BY ELECTROLYSIS[1]

The electrolytic method of determining copper is the most accurate of the gravimetric methods. This deposition may conveniently be made from acid solutions containing free nitric or sulphuric acid or from an ammoniacal solution.

### Rapid Methods

**Rapid Deposition of Copper — Solenoid Method of Heath.** — The solenoid is made by winding 500 turns of No. 13 B and S gauge magnet

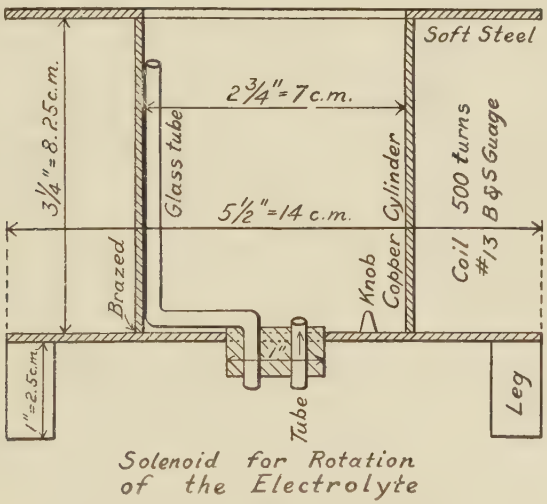



Fig. 68.

wire upon a copper cylinder $2\frac{3}{4}$ in. in diameter, $3\frac{1}{4}$ in. high, $\frac{3}{32}$ in. thickness of metal. The cylinder is brazed water tight at the bottom to a $5\frac{1}{2}$ in. disc of $\frac{3}{32}$ in. soft steel. In this disc is a 1-in. hole for the insertion of a rubber plug, through which glass tubes may be inserted for inlet and outlet of air or water to cool the electrolytic beaker. A steel disc of the same size as the bottom and with an opening to fit is brazed to the top of the cylinder. The solenoid thus made is suitable for a 300 cc. lipless beaker $4\frac{7}{8}$ in. high and $2\frac{1}{4}$ in. diameter. The solenoid coil may be in series in the electrolytic line or excited separately.

The negative electrode is of gauze, 40 meshes per linear inch, with a depositing surface of 100 cm. and is slit to permit quick removal from the electrolyte.

[1] (See method for copper in alloys, page 255).

**Procedure.** — Five grams of the thoroughly cleaned copper sample are dissolved in the covered electrolytic beaker on a steam plate with 40 cc. of stock acid solution composed of 7 parts (1.42 sp.gr.) of nitric acid, 10 parts of sulphuric acid (1.84 sp.gr.) and 25 parts by volume of water. The temperature during the solution is kept just below the boiling point, 50 cc. of the stock solution is used for copper containing 0.03 to 0.1 per cent of arsenic, 60 cc. for material containing 0.11 to 0.5 per cent arsenic. The electrolyte is diluted to 120 cc. A current of 4.5 amperes is used for the electrolysis and the same amount employed to excite the solenoid. During the deposition a double pair of watch glasses cover tightly the beaker until the color of the electrolyte fades out, when they are rinsed and removed. Twenty minutes later and thereafter at 5 minute intervals, a test for completion of deposition is made by withdrawal of 1 cc. onto a porcelain tile and treating with a few drops of freshly prepared hydrogen sulphide water. This test will detect the presence of 0.000005 g. copper or more remaining in the solution. The determination is complete in two and a half hours. Extremely accurate results are obtained when the electrolyte is kept very cold by circulation of water about it and when the cathode is withdrawn within 5 minutes after completion of deposition.

In the assay of casting copper, in case the deposit is evidently impure, the cathode may be stripped by treatment with 50 cc. of the stock solvent and then replated under the conditions described.

Notes. The advantage of the solenoid over any mechanical device for the rotation of electrodes is due to the prevention of loss by spraying from the anode, as the beaker can be covered with a double pair of watch glasses.

Results range from 0.003 to 0.01 per cent higher than the author's slow method of assay of refined copper, and is due to platinum from the anode, which is corroded by the influence of heat, nascent nitrous acid and high current.

**Deposition from Nitric Acid Solution.** — The solution should not contain over 2–3 cc. of free concentrated nitric acid. If more than this is present, the solution is evaporated to expel most of the acid, the remainder neutralized with ammonia and the requisite amount of nitric acid added. The solution is diluted to 100 cc., warmed to 50° or 60° C. and electrolyzed with a current of 1 ampere and 2–2.5 volts. Two hours are sufficient to deposit 0.3 gram copper. Since the hot acid acts vigorously on copper, it is necessary to wash out the acid from the beaker before breaking the current.

**Deposition from an Ammoniacal Solution.** — Ammonium hydroxide is added to the solution containing copper until the precipitate, first formed, dissolves. Twenty to twenty-five cc. of ammonium hydroxide (sp.gr. 0.96) are required for 0.5 gram copper or 30–35 cc. for 1 gram. Three to four grams of ammonium nitrate are added and the solution electrolyzed with a current of $ND/100 = 2$ amperes. The electrodes are washed, without breaking the current, until the ammonia and nitrate are removed.

Lead, bismuth, mercury, cadmium, zinc and nickel should be absent from the ammoniacal solution. Arsenic is not deposited. Unless a very pure platinum anode is used, platinum may contaminate the deposit appreciably. Jena or other brand of zinc borate resistance glass should not be used for the electrolytic beaker.

**Rapid Method Using Rotating Electrodes.** — By this method a gram of copper may be deposited in an hour, a higher amperage being used than with stationary electrodes. Either the cathode or anode may be rotated to keep the solution agitated.

The volume of 200 cc. should contain approximately 10% of nitric acid and 1 cc. of sulphuric acid. The solution is electrolyzed by starting with a current of 2 amperes and gradually working up to 3 amperes as the blue color disappears from the solution. At the end of an hour the rotation is stopped but the current is left on. The beaker in which the electrolysis was conducted is quickly lowered from the electrodes and immediately replaced by a beaker of pure water. The current is now shut off and the electrodes removed and immersed in methyl alcohol. The electrodes are passed rapidly over a flame to ignite the alcohol and this burned off keeping the electrodes in motion to avoid overheating. After cooling in a desiccator the electrodes are weighed. Copper will deposit on the cathode. If lead is present in the solution it will be deposited on the anode as $PbO_2$. The solution should be tested for copper (and lead) by further electrolysis with fresh electrodes. Any additional deposit being weighed and added to previous weights obtained.

## SLOW METHODS

### Electrolytic Determination of Copper in Blister Copper

The sample should be about 20 mesh. Because fine particles are comparatively poor in copper, extreme care must be taken in drawing the portion for analysis to preserve the ratio of the coarse to fine. Some analysts, to avoid sampling error, sieve the coarse from the 40 or 60 mesh fine and either make a separate analysis of each weighed product, or weigh into a single test the due proportion of each. Others draw a large portion, by means of a riffle

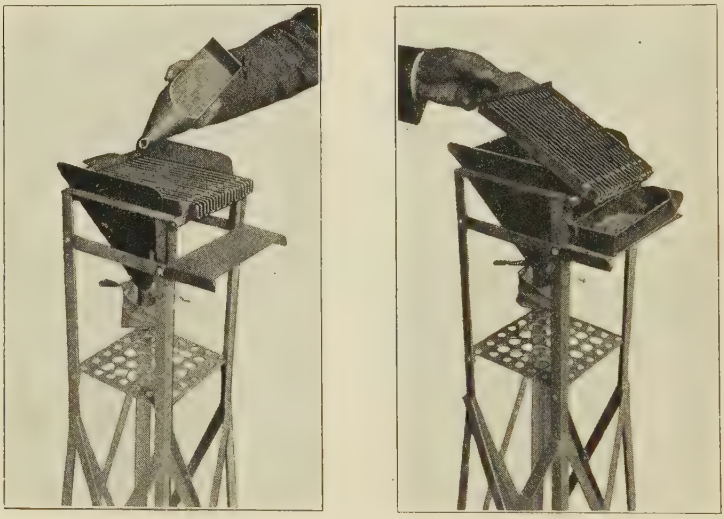


Fig. 69 and 69a. — Riffle Sampler.

(Fig. 69) or similar sampling device and from its solution in a volumetric flask, pipette an aliquot part equivalent to one or more grams.

By the small portion method insoluble matter must be removed by filtration. When the sample contains an insignificant quantity of insoluble matter, the practice is to deposit the silver with the copper and make a correction for its presence in accordance with the result of the silver assay of the sample.

By the large portion method, insoluble matter and silver, as silver chloride, is removed from the electrolyte by sedimentation in the volumetric flask.

**Procedure. — Small Portion Method.** — The coarse and fine portions are quartered down to convenient amounts and from these a 5 gram

composite weighed, which contains the coarse and fine portions in ratio of their percentage weights. The sample is placed in a 350 cc. tall-form beaker, without lip and with flaring rim. Fifty cc. of chlorine-free, stock acid solution (15 parts of nitric and 5 parts of sulphuric acids) are added, the beaker covered with a funnel (stem up), which just fits in the rim, and the mixture heated gently at first and finally to boiling. When the sample has dissolved, 5 cc. of saturated solution of ammonium nitrate are added and the sample diluted to 200 cc. with water.

When the electrolyte has cooled to room temperature the electrodes are introduced, the beaker covered with split watch glasses

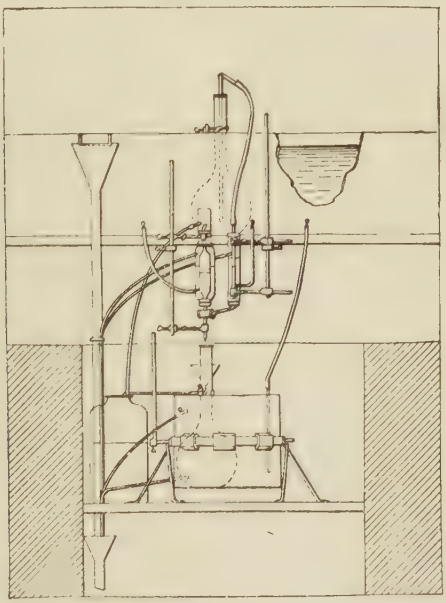


Fig. 70. — Constant Temperature Bath and Dividing Pipette.

and electrolysis started with a current of .05 ampere and continued until the appearance of the foil indicates that the silver has deposited. The current is then raised to ND/100 = .75 ampere and this continued for twenty to twenty-two hours, or until the appearance of gas about the negative electrode indicates that deposition of the copper is practically complete. For the unexperienced a simple method is to add a little water to the electrolyte without breaking the current and after 15 minutes to observe whether any deposition of copper takes place on the freshly exposed surface. The watch glasses and electrode stems should be rinsed when the electrolysis has continued 15–16 hours.

**Procedure. — Large Portion Method.**[1] — The sample is quartered by a riffle sampler (see Fig. 69) to an amount very close to 80 grams. This quantity is weighed and transferred by a paper chute into a 2000 cc. flask, which has been calibrated by the method of repeated delivery at constant temperature of a 50 cc. overflow dividing pipette (see Fig. 70). The liquid employed in calibrating is a copper solution of the same composition as that for which the flask is to be used. A cold mixture of 80 cc. of sulphuric acid (sp. gr. 1.82) and 200 cc. of nitric acid (1.42) with 500 cc. of water is added. A standard solution of sodium chloride is added in sufficient quantity to precipitate the silver, care being taken to add less than 20% excess. A bulbed condenser tube is placed in the neck before putting the flask on a hot plate.

The solution is gradually heated to boiling and when the solution is nearly complete, boiled gently for one hour. This generally completely dissolves the copper present. Residues of lead, tin, silver, or silica if present in appreciable amounts are separated at this point by filtration.

When the solution in the flask has cooled for half an hour, water is added to a little above the 2000-cc. mark, giving the flask a rotary motion during the addition to mix the solution. The flask is placed in a large tank, Fig. 70, containing water and allowed to remain until it becomes of the same temperature as the water and very close to that of the room. The solution is then made exactly to the mark and allowed to settle, after thorough mixing, by placing the flask again in the water tank.

**Electrolysis.** — Portions equivalent to 2 grams of sample are measured out by means of a dividing pipette, with water-jacket through which the tank-water flows. The solution is run into glasses, hydrometer-jar in shape, with concave bottoms, height of glass, $6\frac{1}{2}$ in., diameter $2\frac{1}{6}$ in., Fig. 71. Each portion is treated with 5 cc. of a saturated solution of ammonium nitrate and diluted to 125 cc. with water. ($NH_4NO_3$ or $(NH_4)_2SO_4$ delays deposition of As and Sb until electrolyte is freed from Cu.) The electrolyte, at this stage, contains about 3.7 cc. of nitric acid.

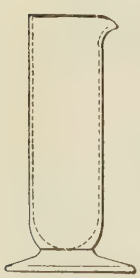


Fig. 71.

The copper is deposited by electrolysis, using a current of .33 ampere per 100 sq.cm., which is kept constant until deposition is complete, about twenty hours. It is advisable to begin the electrolysis in the evening, 5 p.m. The following morning, the inside of the jar, the rods of the electrodes, and the split watch-glasses which cover the jar are rinsed with a spray of water into the glass and the run continued for two or three hours. Each electrode is quickly

[1] W. C. Ferguson, Jour. Ind. and Eng. Chem., May, 1910.

detached from the binding posts, the cathode plunged into cold water, then successively into three jars of 95% alcohol, shaken free of adherent drops and dried by revolving rapidly over a Bunsen flame for a few seconds after ignition of the film of alcohol.

The weighing of foil plus the deposit is made with as little delay as possible.

**Determination of the Copper Remaining in the Electrolytes.** — Since the exhausted electrolyte seldom contains over 0.01% copper, this residual copper can be closely estimated by observation of the depth of the sulphide precipitate. Should circumstances be such that the quantity be more than can be estimated by the appearance of the sulphide precipitate and a determination without rerun is necessary, the precipitate is filtered, incinerated, dissolved with a little hot $HNO_3$, made ammoniacal and after settling, filtered through asbestos. The color of the solution is compared with a standard solution treated with the same amount of reagents as the sample, care being taken that similar conditions prevail when making comparison.

## Notes and Precautions

**Character of the Deposits.** — The ideal deposit is of a salmon-pink color, silky in texture and luster, smooth and tightly adherent. A slightly spongy and coarsely crystalline deposit, although good in color and perfectly adherent, will invariably give high results. A loosely adherent deposit caused by either too rapid a deposition at the commencement or too low a current density at some period of the electrolysis, usually shows a red tint and may give a high result on account of oxidation or a low result because of detachment of particles. A darkly shaded deposit indicates the presence of impurity in greater or less extent. If it is impossible to complete the electrolysis without this appearance the electrolyte should be purified. Impurities such as arsenic, antimony, bismuth, selenium and tellurium may occur in the blister copper.

A dark colored, but perfectly adherent deposit is dissolved very slowly from the foil, in a covered electrolytic jar, by gently heating for several hours with about 60–70 cc. of a solution containing 2 cc. of sulphuric and 5 cc. of nitric acids. When the solution is complete the temperature is raised to expel dissolved gases. Five cc. of saturated ammonium nitrate solution is added and the electrolyte diluted to 125 cc. When cooled to room temperature, electrolysis is carried out under the same conditions as that of the first deposit and on the same foil, if arsenic or antimony is the interfering impurity; on a fresh foil if selenium or tellurium has been the contaminating element. The undeposited copper is determined colorimetrically in the mixture of the first and final electrolytes and added to the weight of the copper deposited.

If the sample contains a large percentage of arsenic or antimony, a portion representing 2 grams is drawn from a pipette into a Kjeldahl flask, 10 cc. of sulphuric acid added, and the liquid evaporated to fumes to expel nitric acid. From this solution cuprous-thiocyanate is precipitated according to the method described on page 243. The funnel containing the filter is placed in a 500 cc. flask with long neck, the filter is punctured and the precipitate washed into the flask with the least quantity of water possible, the adherent precipitate is dissolved from the filter with warm dilute nitric acid, added cautiously to avoid violent evolution of gases from the dissolving precipitate in the flask. The washed filter is incinerated and the solution of its ash by nitric acid added to the electrolyte after completion of electrolysis. When solution of the precipi-

tate is complete, the liquid is boiled to small volume, neutralized, and 5 cc. of ammonium nitrate solution and 3 cc. of excess free nitric acid added. The liquid is transferred to an electrolytic jar and electrolysis carried out in the manner already described.

The amounts of bismuth, arsenic, antimony, selenium or tellurium usually found in blister copper may be separated together with iron present by addition of ammonia to a pipetted portion. The filtered precipitate is purified of copper by solution with nitric acid and reprecipitation. The combined filtrates are neutralized, $3\frac{1}{2}$ cc. of free nitric acid added and the solution electrolyzed under the conditions already described. The nitric acid solution of the incinerated filter, carrying the iron, etc., is added to the electrolyte, after electrolysis is complete, for determination as undeposited copper. The undeposited copper is determined colorimetrically.

The deposited copper is never absolutely pure. The total impurities seldom exceed 0.03%. Ag from 0.000 to 0.18%; As from 0.000 to 0.003%; Sb from 0.000 to 0.004%; Se and Te from 0.001 to 0.027%; Bi from 0.000 to 0.003%. Periodical complete analyses may be made and corrections applied to the analysis when exceedingly accurate percentages are required.

Too low a current density or excessive oxidizing power of the electrolyte may produce high results, due to the oxidation of the deposited copper. Too high a current density or a deficiency of oxidizing power in the electrolyte, by causing a deposition of impurities, will give high results.

The electrodes used by the Nichols Copper Co. are straight platinum wires for the positive ends and cylinders $1\frac{3}{4}$ in. long, 1 in. in diameter of 0.004 in. irido-platinum foil, $11\frac{1}{2}$ sq. in. depositing surface, for the cathodes.

A uniform current is essential.

The nitric acid used should be free of iodic acid.

The presence of oxide of nitrogen gases, or a chloride in an acid solution, will cause a coarsely crystalline or brittle deposit, under conditions which in their absence would produce a good plating. The deposit moreover may contain platinum from the anode if the electrolyte contains a chloride salt.

Silver may be deposited with the copper and correction made for its presence from the result of a separate assay. Copper deposits in poor form, unless the silver be first plated out at a very low current density, about 0.03 Amp. $ND_{100}$.

Solid matter, unless removed, will contaminate the deposit mechanically.

Arsenic, antimony, selenium or tellurium have an influence on the physical character of the deposit which may affect the copper result beyond the sum of such impurities deposited.

Whether impurities are deposited or not, appreciably high results are obtained by continuing electrolysis for some time after the electrolyte has become impoverished of copper.

Overheating of the copper deposit, in the process of ignition of the alcohol clinging to the cathode, will cause oxidation of the copper. As much as possible of the alcohol must be shaken off before passing the electrode rapidly through the flame. It is advisable to weigh the copper shortly after deposition, as prolonged contact with air is undesirable, if extreme accuracy is desired.

The copper deposits may be removed by plunging the electrode, for a few moments, in hot nitric acid. After washing with water, the foil is ignited to a cherry red in a direct colorless flame. The ignition removes any grease which would be objectionable, that may contaminate the platinum. Alcohol frequently contains oily matter which will cling to the electrode in spite of the rapid ignition for drying the deposit.

## VOLUMETRIC METHODS FOR THE DETERMINATION OF COPPER

### POTASSIUM IODIDE METHOD

The procedure depends upon the fact that cupric salts when treated with potassium iodide liberate iodine, the cuprous iodide formed being insoluble in dilute acetic acid.

**Reactions.** $2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2$.
or $2Cu(C_2H_3O_2)_2 + 4KI = Cu_2I_2 \downarrow + 4KC_2H_3O_2 + I_2$.

The liberated iodine is titrated with standard thiosulphate.

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

This method is exceedingly accurate. Very few metals interfere. Bismuth, selenium, trivalent arsenic, antimony or iron should not be present. Lead, mercury, and silver increase the consumption of iodide, but otherwise interfere only because of the color of their iodides.

**Standardization of Sodium Thiosulphate.** — Make up the reagent according to one of the following strengths, as desired.

N/10 solution contains 24.82 grams $Na_2S_2O_3.5H_2O$ per liter. According to the reaction above 1 cc. of this will be equivalent to 0.006357 g. Cu.

If a solution is desired so that 1 cc. = 0.001 g. Cu, dissolve 3.92 grams of the $Na_2S_2O_3.5H_2O$ crystals per liter (248.2 ÷ 63.57). If a 0.5 gram sample is to be taken it is convenient to have the reagent of such strength that 1 cc. is equivalent to 0.005 g. Cu so that 1 cc. is equivalent to 1% Cu. $3.92 \times 5 = 19.6$ *grams* of thiosulphate crystals are required. The addition of 2–4 grams NaOH per liter is claimed to preserve the solutions.

**Standardization. — Copper Method.** — If either a N/10 reagent or the one containing 19.6 grams of the salt are being standardized weigh 0.2–0.25 gram of pure copper (electrolytic), (not over 0.1 gram should be taken for the weakest solution). Dissolve the copper in about 5 cc. of nitric acid (in a flask or a covered beaker), boil to expel brown fumes, dilute to about 50 cc., add ammonia in slight excess (10–12 cc. is generally sufficient), boil until the odor of ammonia is faint and add 5 cc. glacial acetic acid, or sufficient to make the solution acid (test with litmus) and again boil for about one minute. Cool and add to the cold solution 6 cc. of a 50% potassium iodide solution or about 3–4 grams of the solid, and titrate with the standard thiosulphate reagent. The iodine that is liberated (see reaction above) colors the solution brownish; on addition of the thiosulphate the color fades; when the color has changed to yellow, add starch solution

and complete the titration adding the thiosulphate until the blue color (lilac at end) fades out with an added drop of the reagent.[1]

Divide the weight of copper taken by the cc. of reagent required and the result is the weight of copper represented by one cc. of the reagent. An exactly N/10 solution is equivalent to 0.006357 g. Cu.

**Standardization with Permanganate.** — The reagent may be standardized against N/10 potassium permanganate or a permanganate solution whose iron equivalent is known. To about 40 cc. of the N/10 permanganate solution add 6 cc. of the potassium iodide (50%) reagent and titrate the liberated iodine in presence of acetic acid exactly as is described above. 1 cc. of N/10 permanganate should equal 1 cc. of the N/10 thiosulphate. Establish its normality by converting the permanganate to exact cc. in normality equivalent and dividing the cc. by the cc. of thiosulphate required. If preferred multiply the iron equivalent by $\frac{63.57}{55.84} = 1.139$ to get the copper equivalent.

## PROCEDURE FOR COPPER IN ORES

**Solution of the Sample.** — Weigh 0.5 gram of the powdered ore (if a N/10 thiosulphate reagent is to be used, the factor weight 0.636 gram of ore is convenient so that 1 cc. of the reagent is equivalent to 1% Cu). Dissolve in 10 cc. hydrochloric acid and 5 cc. nitric, heating gently to effect solution, adding more of the acids if necessary. Add 10 cc. of sulphuric acid and evaporate to fumes. Heat until any free sulphur that precipitates disappears. Allow to cool. Dilute with 30–40 cc. of water, heat to boiling and keep hot until ferric sulphate has dissolved (copper will all be in solution). Filter into a small beaker and wash the residue at least six times with hot water, using small portions at a time. The volume of the filtrate need not exceed 75–100 cc. This contains all of the copper.

**Precipitation of Metallic Copper.** — Place in the beaker containing the copper solution a piece of heavy sheet aluminum (1.5 inches square) or a bent strip of aluminum bent in form of a triangle, or add 1–2 grams of pure granulated aluminum. If a sheet is used, bend the corners at right angles so it will not lie flat in the beaker. (The sheet may be used repeatedly as it is not attacked to any great extent by the nitric acid subsequently used). Heat the solution to boiling (beaker covered) and keep at this temperature for about 10 minutes. Practically all of the copper will precipitate except a mere trace. If the action is sluggish add 2 or 3 drops of hydrochloric acid. Wash down the cover and sides of the beaker

[1] The addition of a few drops of a weak $AgNO_3$ solution makes the end point sharp. (Suggestion of A. H. Low.)

with hydrogen sulphide water. (This precipitates the trace of copper in the solution and prevents oxidation of the copper).

**Isolation of Copper.** — Decant the solution through a filter and rinse the metallic copper into the filter with a jet of the hydrogen sulphide water, leaving the aluminum as clean as possible in the beaker. Save this. Wash the precipitate 6 times with hydrogen sulphide wash water, allowing to drain, but following up immediately with more solution, until the washing is complete. (Copper is apt to oxidize if allowed to stand exposed to the air. Hence the washing should be completed as soon as possible.)

**Solution of the Copper.** — Punch a hole in the filter and wash the copper into a beaker with a jet of water using as little as possible. (If much copper is present, open the filter on a watch glass and wash the precipitate into a beaker. Again fold the filter and place in the funnel over the beaker.) Pour 5 cc. of strong nitric acid over the aluminum which still contains a little of the copper. When all of this has dissolved pour the nitric acid solution over the filter, catching the acid in the beaker containing the bulk of the copper. (Removing the beaker, place the one containing the foil under the filter.) Cover the beaker containing the copper and boil until the metal is in solution and again place under the filter funnel. Wad the filter paper loosely in the funnel. Pour over this filter 5–10 cc. of bromine water, catching the solution in the beaker containing the copper; this should impart a yellow color to the copper solution. Wash the filter 6 times with water, pouring the water first into the beaker with the aluminum and from this over the wadded filter.

**Concentration.** — Boil the combined solution down to about 25 cc. The bromine will be expelled. Add a small excess of ammonia; the free acid is neutralized and the solution smells of ammonia. Again boil to expel the excess of ammonia. The solution should still smell faintly of $NH_3$. Add glacial acetic acid until slightly acid (litmus test); 5 cc. should be sufficient. Cool thoroughly.

**Potassium Iodide Treatment and Titration with Thiosulphate.** — To the cold solution add 5–6 cc. of 50% solution of potassium iodide and titrate the liberated iodine with standard thiosulphate until the brown color changes to yellow, add starch and complete the titration.

$$1\text{cc. } N/10\ Na_2S_2O_3 = 0.00636 \text{ g. Cu.}$$

### FERROCYANIDE METHOD FOR SMALL AMOUNTS OF COPPER

By this colorimetric method it is possible to detect one part of copper in 2,500,000 parts of water. The procedure depends upon the purplish to chocolate-brown color produced by potassium ferrocyanide and copper in dilute solutions. The procedure is applicable to the determination of copper in water and may be used in presence of a number of elements that occur in slags. Iron also produces a colored compound with ferrocyanide (1 part Fe detected in 13 million parts $H_2O$), so this element must be removed from the solution before testing for copper.

**Solutions. — Standard Copper Solution.** 0.393 gram $CuSO_4.5H_2O$ per liter, 1 cc. = 0.0001 gram Cu.

**Ammonium Nitrate.** — 100 grams of the salt per liter.

**Potassium Ferrocyanide.** — Four grams of the salt per 100 cc.

**Procedure.** — A volume of 5 to 20 drops of potassium ferrocyanide, according to the amount of copper present in the solution, is placed in a tall, clear, glass cylinder or Nessler tube of 150 cc. capacity, 5 cc. of ammonium nitrate solution added and then the whole or an liquot portion of the neutral solution of the assay. The mixture is diluted to 150 cc. The same amount of ferrocyanide and ammonium nitrate solutions are poured into the comparison cylinder, placed side by side with the one containing the sample, on a white tile or sheet of white paper. The standard copper solution is now run from a burette into the comparison cylinder, stirring during the addition, until the color matches that of the assay. The number of cc. required multiplied by 0.0001 gives the weight of copper in the sample contained in the adjacent cylinder.

(Amount of Cu × 100) ÷ wt. sample = % Cu in the sample.

Notes. The solution must be neutral, as the copper compound is soluble in ammonium hydroxide and is decomposed by the fixed alkalies. If the solution contains free alkalies, it is made slightly acid and then the acid neutralized with ammonia, added in slight excess. This is boiled to expel the excess of ammonia, and then tested according to the directions under "Procedure." Solutions containing free acids are neutralized with ammonia.

Iron may be removed by precipitation with ammonia. As this hydroxide occludes copper, the precipitate should be dissolved and reprecipitated to recover the occluded copper.

*Determination of copper in water* is accomplished by evaporating a quantity of water to dryness, taking up the residue with a little water containing 1 cc. of nitric acid, the residue having been ignited to destroy organic matter, precipitating iron with ammonia, and determining copper in the filtrate.

### Ammonia Method for Determining Small Amounts of Copper

In the absence of organic matter, nickel and elements giving a precipitate with ammonia, copper to an upper limit of 10 milligrams can be determined by comparison of the depth of the blue tint of its ammonium solution with a temporary or permanent standard copper solution of equal volume.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Determination of Copper in Refined Copper

In determining the quality of copper for electrical purposes each hundredth of a percent above 99.90 has its significance. The methods employed are the electrolytic and the hydrogen reduction methods. Silver present is rated as copper.

Fig. 72

**Electrolytic Method.** — The sample, consisting of unground drillings, should be untarnished, free of grease or oil, and cleaned of particles of iron by use of a good magnet.

**Procedure.** — A catch weight of about 5 grams is taken, each piece being examined for dust, particles from the drill and surface oxidation before it is placed on the balance pan. Solution is effected in a special 400 cc. beaker which has hipped sides to support a series of watch glasses, the lower hip at the 125 cc. mark, the upper at 350 cc. (Fig. 72.)

The drillings are treated with 50 cc. of a stock solution (10.5 parts of nitric acid and 4.5 parts of sulphuric). The watch-glass traps are put in place to retain the copper which is always entrained in the nitrogen peroxide fumes. Except that the current is maintained at .75 ampere throughout the period of electrolysis, the conditions are the same as have been described for the determination of copper.

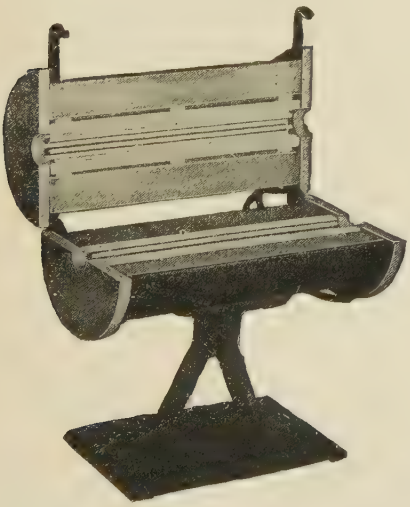


Fig. 73. — Combustion Furnace, Hinged Design, Type 70 — Shown with one "Spare" Unit. Height to center, 9½".

By courtesy of the Electric Heating Apparatus Company, New York City.

**Hydrogen Reduction Method.** — This method is applicable to the determination of copper in grades of refined copper which are characterized by a metallic impurity content which is constant and less than 0.01 per cent. The apparatus consists of a combustion furnace, preferably electrolytically heated, the temperature of which can be kept constant at about 950° C.; a silica tube of 3-in. bore, one end of which is connected with a large Peligot tube containing concentrated sulphuric acid, the

other end connected by a rubber plug and flexible tube with a source of purified hydrogen; porcelain combustion boats 95 mm. long, 18 mm. wide and 10 mm. deep.

**Procedure.** — A catch weight of about 25.1 grams of drillings is placed in the combustion boat, and the boat inserted in the silica tube. After passing hydrogen for half an hour through the cold tube, the temperature is raised to 950° C. and so maintained for two hours. If the furnace is of a type which will permit the removal of the tube without disconnecting the train,[1] the tube is taken from the furnace without interruption of the stream of hydrogen and cooled by a jet of cold air. When cold, the mass of copper, the particles of which are cemented, is taken from the boat and weighed.

NOTE. If the sample is allowed to become molten, the boat and tube will be coated with a film of copper.

### Determination of Copper in Blue Vitriol

This is best determined on a 2 gram sample of the finely powdered dry salt or a catch weight of approximately 2 grams if the salt is moist. Copper is deposited electrolytically, the electrolyte being diluted to 130 cc. and containing 4 cc. of nitric acid and 5 cc. of saturated solution of ammonium nitrate. A current of .18 amperes and an electrode of $11\frac{1}{2}$ sq. in. depositing surface are used. If the salt contains insoluble matter consisting wholly of basic salts, complete solution is brought about by gently boiling after adding 4 cc. of nitric acid and 25 cc. of hot water to the salt. If the insoluble matter shows a tendency to remain in suspension, the presence of arsenic or antimony is indicated. In this case the impurities are precipitated along with ferric hydroxide as has been previously described under the notes on the electrolytic determination of copper in blister copper.

### Determination of Copper and Lead in Brass[2]

One gram of the alloy is dissolved in 8 cc. of nitric acid and the nitrous fumes are boiled off; if tin is present, 40 cc. of boiling water are added, the metastannic acid allowed to settle on the hot plate for fifteen minutes and filtered off. (Method for tin is accurate only for wrought brass; high iron or antimony interfere.)

The filtrate from the tin is electrolyzed for copper and lead. If the lead is less than 0.75 per cent, an ordinary sandblasted, spiral anode is used; if the amount of lead is 0.75 to 5 per cent a sandblasted

[1] A convenient and efficient type of combustion furnace, hinged design, is shown in Fig. 73. This furnace may be purchased from the Electric Heating Apparatus Company, New York City.

[2] Method of The National Brass and Copper Tube Company, communication by R. T. Roberts.

gauze cylinder is necessary. For amounts of lead over 5 per cent either a smaller sample is taken or the greater part of the lead is precipitated as lead sulphate and the small amount of lead passing into the filtrate is recovered by electrolysis, using $\frac{1}{4}$ ampere current per solution, after adding 3 cc. of nitric acid. For lead under 0.5 per cent 5 cc. of 1 : 1 sulphuric acid are stirred in, after the current has been passing for at least ten minutes. If the lead is high the sulphuric acid is added after the electrolysis has continued for at least an hour. Under these conditions no lead sulphate deposits from the solution and as long as the current passes, the sulphuric acid present does not attack the $PbO_2$ deposited. After the sulphuric acid is added the current is raised to 0.5 ampere per solution and the electrolysis continued overnight.

The lead peroxide is dried at 250° C. for half an hour. The factor 86.43 gives the equivalent per cent of lead. (Factor determined from the average of a large number of tests made on pure lead. The factor is best obtained under the conditions of the laboratory where the determinations are made, as it varies slightly with change of conditions.)

The copper on the cathode is washed, dried and weighed according to the usual standard procedure.

### Copper in Steel, Cast Iron, and Alloy Steels

From 3 to 5 grams of steel, depending upon the amount of copper present, are dissolved in a mixture of 60 cc. of water and 7 cc. of sulphuric acid (sp. gr. 1.84) in a 250-cc. beaker. After all action has ceased, a strip of sheet aluminum, $1\frac{1}{2}$ ins. square, bent so that it will stand upright in the beaker, is placed in the solution.

After boiling the solution for twenty to twenty-five minutes, which is sufficient to precipitate all of the copper in the sample, the beaker is removed from the heat and the cover and the sides washed down with cold water. The liquid is decanted through an 11 cm. filter, the precipitate washed three times with water, then placed with the filter in a 100 cc. beaker, and 8 cc. of concentrated nitric acid and 15 cc. of water are poured over the aluminum and the solution heated to boiling. This hot solution is poured over the precipitate and filter in the 100-cc. beaker, and boiled until the paper becomes a fine pulp, only a few minutes being required. The solution is filtered, the residue washed several times with hot water and copper determined in the filtrate by the electrolytic or iodide methods.[1]

[1] The Editor desires to mention the assistance received from W. G. Derby and Dr. A. H. Low in the preparation of this chapter.

## FLUORINE

**F′, at.wt. 19; D (air) 1.31⁵, sp.gr. (–187°) 1.14; m.p. –223°; b.p. –187° C.; acids, HF, $H_2SiF_6$**

The determination of fluorine in the evaluation of minerals used for the production of hydrofluoric acid is of techical importance. The demand for elimination of the use of fluorides for preservatives of food makes its estimation in small amounts of importance.

Fluorine is the most active element known, and is by far the most active of the halogens, displacing chlorine, bromine, and iodine from their combinations.

### OCCURRENCE

Fluorine occurs only combined. It is found abundantly combined with lime in the mineral fluorspar, $CaF_2$. It occurs as cryolite, $Na_3AlF_6$; apatite, $3Ca_5(ClF)(PO_4)_3$. It is found in mineral springs, ashes of plants, in bones, and in the teeth ($CaF_2$). It occurs sparingly, with aluminum and silicon, in topaz, and with cerium and yttrium in fluocerite, yttrocerite, also in wavellite, wagnerite, etc. The minerals are described in the chapters dealing with the metals combined with fluorine.

FIG. 74 — Hanging Drop Test for Fluorine.

### DETECTION

**The Hanging-Drop Test.** — The test depends upon the reaction $3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3$.

If the material contains carbonates, it is calcined to expel carbon dioxide. Half a gram of the powdered dry material is mixed with 0.1 gram dried precipitated silica and placed in a test-tube, Fig. 74, about 5 cm. long by 1 cm. in diameter. A one-hole rubber stopper fits in the tube. A short glass tube, closed at the upper end, passes through the stopper extending about 3 mm. below. Two or three drops of water are placed in this small tube by means of a pipette, nearly filling it. Two cc. of concentrated sulphuric acid are added to the sample in the test-tube and this immediately closed by inserting the stopper carrying the hanging-drop tube, exercising care to avoid dislodging the drop of water. The test-tube is placed in a beaker

of boiling water and kept there for thirty minutes. If an appreciable quantity of fluorine is present a heavy gelatinous ring of silicic acid will be found at the end of the hanging drop tube in the stopper.

It is important to have material, test-tube, and rubber stopper dry, so that the deposition may occur as stated.

NOTE. Dr. J. C. Olsen makes the test by heating the sample in a small Erlenmeyer flask, with concentrated sulphuric acid. A watch-crystal with a drop of water suspended on its curved surface is placed over the mouth of the flask. A spot etch is obtained in presence of fluorine.

**Etching Test.** — The procedure depends upon the corrosive action of hydrofluoric acid on glass, the acid being liberated from fluorides by means of hot concentrated sulphuric acid. This test is applicable to fluorides that are decomposed by sulphuric acid. The reactions taking place may be represented as follows:

I. $CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$

II. $SiO_2 + 4HF = 2H_2O + SiF_4.$

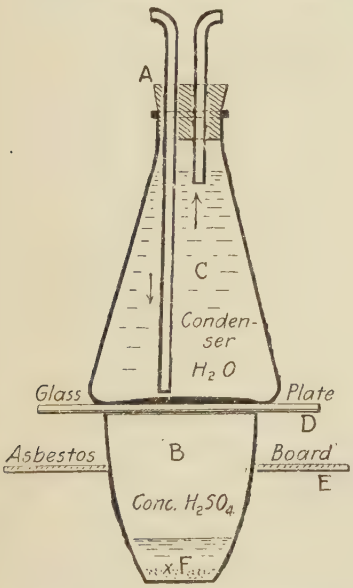



FIG. 75. — Etching Test for Fluorine.

The test may be carried out in the apparatus shown in the illustration, Fig. 75. A clear, polished glass plate 2 ins. square, free from scratches, is warmed and molten wax allowed to flow over one side of the plate, the excess of wax being drained off. A small mark is made through the wax, exposing the surface of the plate, care being exercised not to scratch the glass. If the test is to be quantitative, the marks should be of uniform length and width. The powdered material is placed in a large platinum crucible (*B*) (a lead crucible will do); sufficient concentrated sulphuric acid is added to cover the sample. The plate (*B*) with the wax side down is placed over the crucible and pressed firmly down. To prevent the wax from melting, a condenser (*C*), with flowing water, cools the plate. An Erlenmeyer flask (*C*) is an effective and simple form of condenser, though a metallic cylinder is a better conductor of heat. A little water placed on the plate makes better contact with the condenser. As a further protection a wide collar of asbestos board (*E*) may be placed as shown in the figure. In quantitative work, where a careful regulation of heat is necessary, the crucible is placed in a casserole with concentrated sulphuric acid or in a sand bath, containing a thermometer to register the temperature. The run is best conducted at a temperature of

200° C. (not over 210° — $H_2SO_4$ fumes). After an hour the wax is removed with hot water and the plate wiped clean, and examined by reflected light for etching. A test is positive when the mark can be seen from both sides of the glass. Breathing over the etched surface intensifies the mark.

**Treatment of Fluo-Silicates not Attacked by Sulphuric Acid.** — The powdered material is mixed with about eight times its weight of sodium carbonate and fused in a platinum crucible. The cooled melt is extracted with water. Calcium fluoride is thrown out from the filtrate, according to directions under Preparation and Solution of the Sample. The fluoride may now be tested as directed in the etching test or by the hanging-drop test.

**Black Filter Paper Test.** — According to P. E. Browning, small amounts of fluorine may be detected by the converse method for detection of silicates and fluosilicates (See silicon).

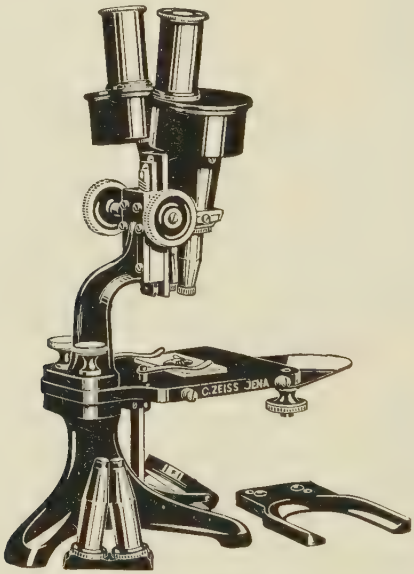



FIG. 75a. — Zeiss Binocular Microscope XA.
(Courtesy of Harold M. Bennett, New York)

## METHODS FOR THE DETERMINATION OF FLUORINE

### Preparation and Solution of the Sample

Fluorides of the alkalies, and of silver and mercury, are readily soluble; copper, lead, zinc, and iron fluorides are sparingly soluble; the alkaline earth fluorides dissolve in 100 cc. of $H_2O$ as follows: $BaF_2$ = 0.163 gram, $SrF_2$ = 0.012 gram, $CaF_2$ = 0.0016 gram.

Fluosilicates of potassium, sodium, and barium are slightly soluble in water and practically insoluble if sufficient alcohol is added.

**Valuation of Fluorspar. — Perchloric Acid Method.** — One gram of fluorspar is treated with 15 cc. of perchloric acid and 15 cc. of water in a suitable distillation flask and heated in an oil bath until the residue is almost dry. The distillation is continued with 10 cc. and finally 5 cc. portions of perchloric acid and equal amounts of water. Hydrofluoric acid may be determined as lead chlorofluoride in the distillate and water soluble residue analyzed for metals.

**Calcium Fluoride.** — The product is best decomposed by fusion with sodium and potassium carbonates or sodium and potassium hydroxide in an iron crucible. If the latter fusion mixture is used, heat first to fusion to expel the water before adding the ore, after mixing the fluoride with 2.5 times as much silicic acid, followed by ten times its weight of carbonates. Most of the silicic acid and all the fluorine will be changed to soluble alkali salts, while the calcium will be left as insoluble calcium carbonate.

**Silicious Ores and Slags.** — 0.5 to 1.0 gram of material is fused in a crucible with ten times its weight of sodium and potassium carbonates (1 : 1) and poured into an iron mould. If a porcelain crucible has been used, this is broken up and added to the cooled fusion. The mass is digested with about 200 cc. of hot water for an hour, the mass having been broken up into small lumps (Kneeland recommends using an agate-ware casserole as diminishing the liability of subsequent bumping) then boiled briskly for ten minutes longer and filtered, the solution being caught in a large beaker. The residue is washed with hot water, followed by a hot solution of ammonium carbonate and the insoluble material rejected. The silica is removed with ammonium carbonate, followed by the zinc oxide treatment of the second filtrate, as described under the section of Separations. In presence of appreciable amounts of fluorides, the gravimetric precipitation of fluorine as calcium fluoride is recommended.

**Removal of Silicic Acid from Fluorides.** — This separation is frequently required, especially in samples where the sodium and potassium carbonate fusion has been necessary for decomposition of fluosilicates, or calcium fluoride mixed with silicic acid.

To the alkaline solution about 5 to 10 grams of ammonium carbonate are added, the solution boiled for five minutes and allowed to stand in the cold for two or three hours. The precipitate is filtered off and washed with ammonium carbonate solution. The fluoride passes into the filtrate, while the silicic acid remains on the filter.

## GRAVIMETRIC METHODS FOR THE DETERMINATION OF FLUORINE

### PRECIPITATION AS CALCIUM FLUORIDE

The method utilizes the insolubility of calcium fluoride in dilute acetic acid in its separation from calcium carbonate, the presence of which facilitates filtration of the slimy fluoride. The reaction for precipitation is as follows:

$$2NaF + CaCl_2 = CaF_2 + 2NaCl.$$

**Procedure.** — Solution of the sample and the removal of silica having been accomplished according to procedures given under Preparation and Solution of the Sample, and Separations, the solution is neutralized, if acid, by the addition of sodium carbonate in slight excess; if basic, by addition of hydrochloric acid in excess, followed by sodium carbonate. To this solution, faintly basic, 1 cc. of twice normal sodium carbonate reagent is added, followed by sufficient calcium chloride solution to precipitate completely the fluoride and the excess of carbonate, i.e., until no more precipitate forms, and then 2–3 cc. in excess. After the precipitate has settled, it is filtered and washed with hot water. (The filtrate should be tested for fluoride and carbonate with additional calcium chloride.) The precipitate of calcium fluoride and carbonate is dried and transferred to a platinum dish, the ash of the filter, burned separately, is added and the material ignited. After cooling, an excess of dilute acetic acid is added, and the mixture evaporated to dryness on the water bath. The lime is converted to calcium acetate, while the fluoride remains unaffected. The residue is taken up with a little water, filtered and washed with small portions of hot water, by which procedure calcium acetate is removed, while calcium fluoride remains on the filter.[1] The residue is dried, separated from the filter and ignited. This, together with the ash of the filter, is weighed as $CaF_2$.

To confirm the result, the residue is treated with a slight excess of sulphuric acid and taken to fumes in a platinum dish. The adhering acid is removed as usual by heating with ammonium carbonate, and the ignited residue weighed as calcium sulphate. $CaF \times 1.7436 = CaSO_4$.

$CaO \times 1.3924 = CaF_2$, or $\times 0.677 = F$. $CaF_2 \times 0.4867 = F$.

[1] The results are slightly low, owing to the solubility of calcium fluoride: 100 cc. of $H_2O$ dissolves 0.0016 gram $CaF_2$; 100 cc. of 1.5 N. $HC_2H_3O_2$ dissolves 0.011 gram.

### PRECIPITATION OF FLUORINE AS LEAD CHLOROFLUORIDE

The method, worked out by Starck, takes advantage of the double halide formed by action of lead chloride upon a soluble fluoride. The compound, PbFCl, is about fourteen times the weight of the fluorine it contains. Unfortunately, the compound is quite appreciably soluble in water,[1] so that a loss occurs if pure water is used for washing the precipitate. The method is limited to the determination of soluble fluorides.

The sample, made neutral, is treated with a large excess of a cold saturated solution (200 cc. of $PbCl_2$ per 0.1 gram of NaF in 50 cc. solution) of lead chloride, the precipitate, settled over night, is filtered off in a weighed Gooch crucible, washed several times with a saturated solution of lead chlorofluoride, and finally two or three times with ice-cold water. The compound is dried two hours at 140–150° C., and weighed as PbFCl.

[1] One hundred grams of $H_2O$ at 18° C. dissolves 0.0325 gram of PbFCl and 0.1081 gram at 100° C.

## VOLUMETRIC METHODS FOR THE DETERMINATION OF FLUORINE

### Volumetric Determination of Fluorine — Formation of Silicon Tetrafluoride and Absorption of the Evolved Gas in Water. Offerman's Method

Silicon tetrafluoride is formed by the action of sulphuric acid upon a fluoride in presence of silica, the evolved gas is received in water and the resulting compound titrated with standard potassium hydroxide. The method is suitable for determining fluorine in fluorspar.

**Reactions:** A. $3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$.
B. $H_2SiF_6 + 6KOH = 6KF + SiO_2 + 4H_2O$.

**Procedure.** — The powdered sample, containing the equivalent of 0.1–0.2 gram of calcium fluoride, is mixed with about three times its weight of pulverized quartz (previously ignited and kept in a desiccator), placed in the decomposition flask *F*, shown in Fig. 76, and about 1 gram of anhydrous copper sulphate added, followed by 25 cc. of concentrated sulphuric acid. The stopcock *E* is closed and the air bath heated gradually till in one-half hour the temperature has risen to 220° C. The cock *E* is now opened and air slowly forced through the apparatus (by means of a water pump) at the rate of about three bubbles per second, the temperature being kept at 220° C., and the flask containing the sample occasionally shaken. When the bubbles of silicon tetrafluoride have disappeared from *F*, the flame is removed, but the air current continued for half an hour longer. The run having been made as directed, the solution in tube *K* is poured into a beaker, an excess of standard potassium hydroxide added and after heating the solution to boiling the excess alkali is titrated with standard sulphuric acid, using phenolphthalein indicator.

Notes. The bottles *A*, *B*, *C*, and *D* are for the purpose of thoroughly drying the air, as moisture in the apparatus is to be avoided. *G* contains strong sulphuric acid, *H* is filled with glass beads to remove sulphuric acid spray, *I* and *J* are empty tubes, which should be thoroughly dry. The gas is completely absorbed in *K*.

It is found advisable to use mercury in the tube *K* as a trap, thus preventing the stoppage of the delivery tube by crystalization. The gas readily passes up through the mercury and is absorbed in the supernatant solution.

In place of using N/10 solutions the potassium hydroxide may be made of such strength that 1 cc. will equal 1 % fluorine with 0.5 g. sample taken and the acid made to a corresponding strength.

Minerals not decomposed with sulphuric acid should be fused with $Na_2O_2$ and the fused mass placed in the generating flask. 50 cc. of conc. $H_2SO_4$ is now added to overcome the NaOH.

## COLORIMETRIC DETERMINATION OF FLUORINE — METHOD OF STEIGER AND MERWIN [1]

The method is based on the bleaching action of fluorine upon the yellow color produced by oxidizing a solution of titanium with hydrogen peroxide. A known amount of titanium in solution is mixed with a definite volume of the solution containing the fluorine and the tint compared with a standard solution containing an equivalent amount of titanium. The extent of bleaching enables the computation of the fluorine present. The method is applicable to determination of fluorine in amounts ranging from 0.00005 to 0.01 gram. Merwin has shown that large amounts of alkali sulphates have a bleaching action similar to fluorine. Addition of free acid, or rise of temperature, intensifies the color lost by bleaching. Aluminum sulphate has no marked effect on standard solutions, or on solutions bleached by alkali sulphates, but it restores the color to a considerable degree to solutions bleached by fluorine. Ferric sulphate has a similar effect. Phosphoric acid bleaches a standard solution. Silica has little effect. According to Merwin an accuracy of 0.002 gram may be expected, an error which is half that of the most reliable gravimetric method.

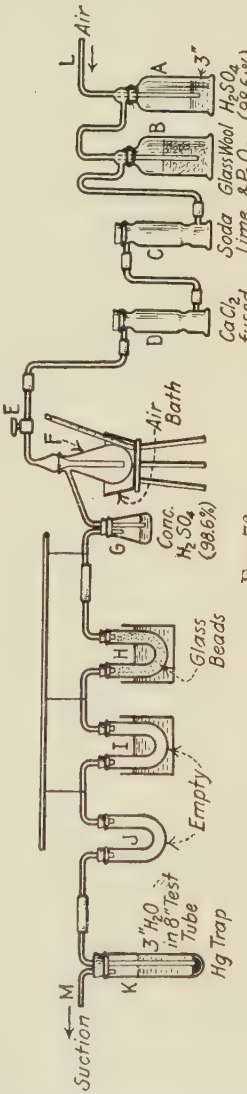



FIG. 76

**Reagents. — Standard Titanium Solution.** — An intimate mixture of 1 gram of $TiO_2$ and 3 grams of ammonium persulphate is heated until the vigorous action has ceased, and the ammonium sulphate is expelled. The residue is treated with 20 cc. of strong sulphuric acid, heated to fuming and, when cold, poured into about 800 cc. of cold water. When the suspended salt has dissolved, 57.5 cc. of strong sulphuric acid are added, and the solution made up to 1000 cc. (50 cc. or more of the solution should be analyzed for $TiO_2$). *One cc. will contain* 0.001 *gram* of $TiO_2$.

**Standard Fluorine Solution.** — 2.21 grams of sodium fluoride, which has been purified by recrystallizing, washing, and igniting

[1] C. Steiger, Jour. Am. Chem. Soc., **30,** 219, 1908. H. E. Merwin, Am. Jour. Sci. 4 (**28,** 119, 1909), Chem. Abs., 3, 2919 (1909). J W. Mellor, "A Treatise on Quantitative Inorganic Analysis." Chas. Griffin & Co.

strongly, is dissolved in 1000 cc. of water. One cc. will contain 0.001 gram of fluorine.

**Sulphuric Acid.** — 95.5% solution, sp.gr., 1.84.

**Hydrogen Peroxide.** — Ordinary strength.

**Standard Colored Solution.** — The solution used in determining fluorine in materials fused with alkali carbonates contains 10 cc. of the titanic solution, 4 cc. of hydrogen peroxide, and 4 cc. of concentrated sulphuric acid.

**Apparatus.— Nessler Tubes** 6 cm. long, 2.7 cm. in diameter are recommended by the authors. Colorimeters may be used in place of Nessler tubes.

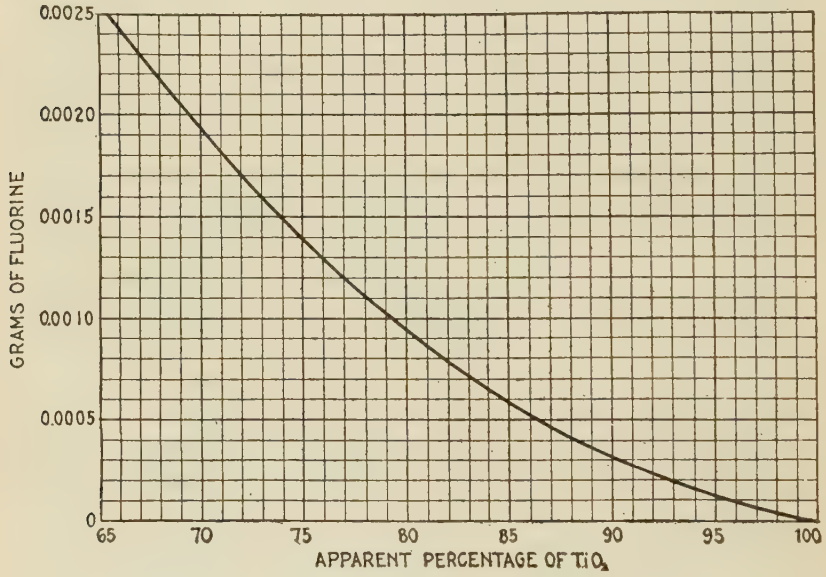



Fig. 77

**Procedure.**— Two grams of the powdered sample are fused with 8 grams of mixed sodium and potassium carbonates, the fusion taken up with hot water, and when leached, 3 to 4 grams of ammonium carbonate added. The mix is warmed for a few minutes and then heated on the water bath till the ammonium carbonate is decomposed and the bulk of liquid is small. Silica, ferric oxide, and aluminum oxide are thrown down and are removed by filtration. The filtrate, which should not exceed 75 cc., is treated with 4 cc. of hydrogen peroxide, and then 10 cc. of standard titanium solution cautiously added ($H_2O_2$ prevents precipitation of $TiO_2$ by the alkali carbonates), followed by 4 cc. of strong sulphuric acid to neutralize the alkali carbonates. The solution, neutral or slightly acid, acquires a light

orange tint. A little sodium carbonate is added in just sufficient amount to discharge the color, and then a drop or so of acid to again restore it. The amount of excess acid now required depends upon the amount of fluorine present in the solution. For amounts of fluorine less than 0.0025 gram (0.125% of sample), 3 cc. of $H_2SO_4$ are added. For amounts of 0.0025 to 0.012 gram of fluorine, 12 cc. of acid are added. The solution is diluted to 100 cc. and cooled to 22° C.

**Comparison.** — The test solution is now compared with the standard solution containing 10 cc. of titanium reagent, the temperature, amount of acid and hydrogen peroxide being the same as the test sample (volume of 100 cc.). If Nessler tubes are used, these are held over a white surface illuminated with diffused light. In the absence of a bleaching substance, such as fluorine, the two solutions will have the same tint,

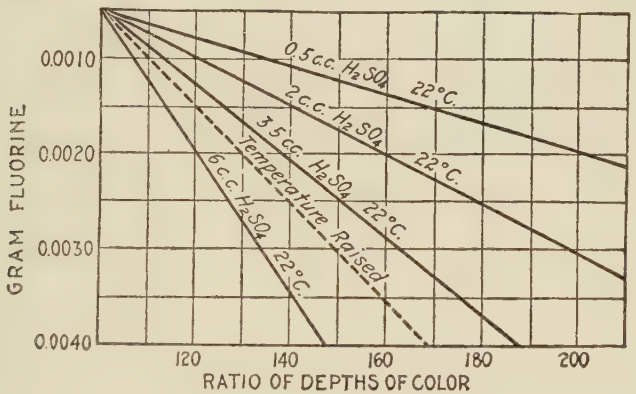



Fig. 77a.

but in presence of fluorine the bleaching effect will cause the test solution to appear paler than the standard. The depths of the liquids are adjusted so that the tubes will have the same intensity of color when moved from right to left or reversed. Should the left eye perceive a darker shade, the tube on the left will appear uniformly darker whether it be the test sample or the standard. The comparative depths or volumes of the liquids in the tubes are measured and the ratio obtained by dividing the depth or volume of the fluorine solution by the depth or volume of the standard and multiplying by 100. Reference may be made to the plotted curve shown in Fig. 77. The ratio $\frac{\text{Depth of F Sol.}}{\text{Depth of Standard}} \times 100 =$ the abscissa, while the ordinate represents the amount of fluorine in the 2 gram sample.

**Example.** — Suppose the test solution = 3.6 cm. and the standard = 4.5 cm., the ratio then = 80, from the curve it is evident that the fluorine = 0.00095 gram or 0.0475%, since a 2 gram sample was taken.

## NOTES

1. The destruction of ammonium carbonate is necessary because ammonium sulphate bleaches the final solution and should be absent.

2. Changes of temperature of 50° C. intensify the color 5 to 15 per cent.

3. Increasing the acidity tends to restore the bleached color.

4. The same ratios are obtained by dividing the final volume of the standard by the volume of the test in cases in which a colorimeter is used which requires the standard to be diluted.

5. According to Merwin, however, the bleaching effect of alkali sulphates, which are present, will make the ratio much higher than it would be if they were absent. (The sulphates alone give a ratio of 125.) This ratio should be determined on two 8-gram portions of the alkali carbonate mixture used in the fusion and the correction made accordingly. If this ratio is represented by m and r is the ratio of the two solutions, then $(r - m) \div 23{,}000 =$ g. F. for amounts of fluorine not exceeding .0025 g. (3 cc. $H_2SO_4$, 22° C., 4 cc. $H_2O_2$, .01 g. $TiO_2$). If the fluorine amounts to .0025 to .012 g. then 12 cc. $H_2SO_4$ is added and the formula required is $(r - m - 3) \div 6{,}300 =$ g. F. (m blank should be determined and should not much exceed 108). In absence of sulphates the following formula are given —

(*a*) $(r - 100) \div 70{,}000 =$ g. F, with .5 cc. $H_2SO_4$, limits of F = .00005 to .001 g.

(*b*) $(r - 100) \div 22{,}000 =$ g. F, with 3.5 cc. $H_2SO_4$, limits of F = .001 to .004 g.

Example (*a*) if r = 142 then $(142 - 100) \div 70{,}000 = .0006$ g. F.

## DETERMINATION OF TRACES OF FLUORINE

An approximate estimation of traces of fluorine may be made by utilizing the method outlined for detection of this element. By varying the amounts of substance tested an etch is obtained that is comparable with one of a set of standard etches, obtained with known amounts of fluorine in form of calcium fluoride, added to the same class of material examined.

The conditions in obtaining the standard etches and those of the tests should be the same. This applies to the temperature of the paraffine bath, duration of the run, size of mark exposing the surface of the test-plate, and the general mode of procedure.

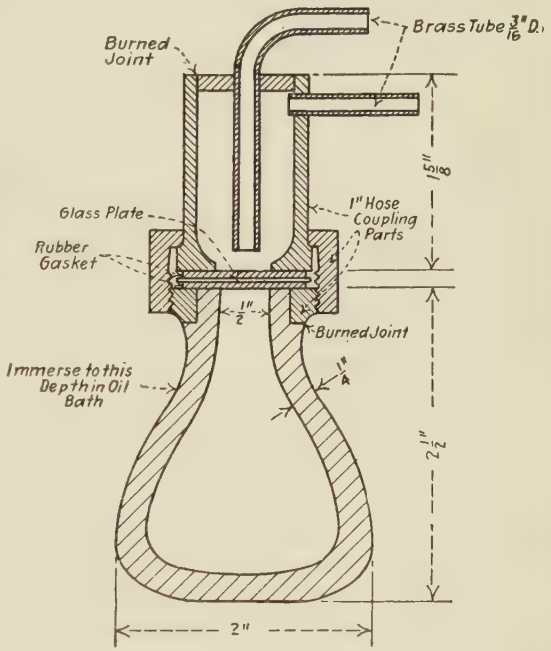



FIG. 78

One gram of sample is placed in a lead bomb with 12 cc. of sulphuric acid, the bomb closed with glass plate in place and heated in an oil bath for 45 minutes at 165° C. The etching on the glass plate is compared with etching using known amounts of fluorine as $CaF_2$ and the same kind of glass.

The glass plate is kept cool by circulating cold water. The type of bomb and its connections are shown in figure 78.

NOTE. The importance of regulating the temperature may be seen by the results obtained by Woodman and Talbot. With a temperature of 79–80° C., one part of fluorine may be detected in 25 to 100 thousand parts of material; by raising the temperature to 136° C., the delicacy of the procedure is increased to one part of fluorine in 1 to 5 million parts. The limit of delicacy is apparently reached at 213–218° C. (i.e., 1 part F per 25 million).

A metal condenser, such as is recommended for mercury determinations, may be used and the oil or paraffine bath substituted by an electric heater automatically controlled.

Crisco is claimed to be better than paraffine, as this does not give off any unpleasant fumes when heated.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### VALUATION OF FLUORSPAR

The following procedure meets the commercial requirements for the valuation of fluorspar. The determinations usually required are calcium fluoride, silica, and calcium carbonate; in some particular cases lead, iron, zinc, and sulphur.

**Procedure. — Calcium Carbonate.** — One gram of the finely powdered sample is placed in a small Erlenmeyer flask, 10 cc. of 10% acetic acid are added, a short-stemmed funnel inserted in the neck of the flask as a splash trap, and the mixture heated for an hour on a water bath, agitating from time to time. The calcium carbonate is decomposed and may be dissolved out as the soluble acetate, whereas the fluoride and silica are practically unaffected. The solution is filtered, through a 7 cm. ashless filter, the residue washed with warm water four times, and the filter burned off in a weighed platinum crucible at as low a temperature as possible. The loss of weight minus 0.0015 gram (the amount of calcium fluoride soluble in acetic acid under the conditions named) is reported as *calcium carbonate.*

**Silica.** — The residue in the platinum crucible is mixed with about 1 gram of yellow mercuric oxide, in form of emulsion in water (to oxidize any sulphide that may be present); any hard lumps that may have formed are broken up, the mixture evaporated to dryness and heated to dull redness, then cooled and weighed. About 2 cc. of hydrofluoric acid are added and the mixture evaporated to dryness. This is repeated twice to ensure complete expulsion of silica (as $SiF_4$). A few drops of hydrofluoric acid are then added, together with some macerated filter paper, and a few drops of ammonium hydroxide to precipitate the iron. The solution is evaporated to dryness, heated to dull redness, cooled and weighed. The loss of weight is reported as *silica.*

**Calcium Fluoride.** — The residue is treated with 2 cc. of hydrofluoric acid and 10 drops of nitric acid (to decompose the oxides), the crucible covered and placed on a moderately warm water-bath for thirty minutes, the lid then removed and the sample taken to dryness. The evaporation with hydrofluoric acid is repeated to ensure the transposition of the nitrates to fluorides, and if the residue is still colored, hydrofluoric acid again added and the mixture taken to dryness a third time; then a few drops of hydrofluoric acid are added and 10 cc. of ammonium acetate solution (the acetate solution is made by neutralizing 400 cc. of 80% acetic acid with strong ammonia, adding 20 grams of citric acid and making the mixture up to 1000 cc. with strong ammonium hydroxide). The mixture is digested for thirty minutes on a boiling water bath, then filtered and washed with hot water containing a small amount of ammonium acetate, and finally with pure

hot water. (Several washings by decantation are advisable.) The residue is ignited in the same crucible and weighed as *calcium fluoride.* An addition of 0.0022 gram should be made to compensate for loss of $CaF_2$.

Pure calcium fluoride is white. To test the purity of the residue, 2 cc. of sulphuric acid are added and the material taken to fumes to decompose the fluoride; 1 cc. of additional sulphuric acid is added and the excess of acid expelled by heating. The residue is weighed as calcium sulphate. This is now fused with sodium carbonate, and the fusion treated with hydrochloric acid in excess. If barium is present the solution will be cloudy (= $BaSO_4$).

## ANALYSIS OF SODIUM FLUORIDE

**Preparation of the Sample and Insoluble Residue.** — Ten grams of the sample are dissolved in 250 cc. of water in a beaker, and boiled for five minutes, then filtered into a liter flask through an ashless filter; the residue is washed with several portions of water and ignited. This is weighed as insoluble residue. The filtrate and washings are made to 1000 cc. with distilled water.

**Sodium Fluoride.** — Fifty cc. of the solution equivalent to 0.5 gram of sample are diluted to 200 cc. in a beaker, 0.5 gram sodium carbonate is added and the mixture boiled. An excess of calcium chloride solution is now added slowly and boiled for about five minutes. A small amount of paper pulp is added to prevent the precipitate from running through the filter, the precipitate allowed to settle and then filtered, using a 9 cm. fine grain filter paper. The fluoride is washed twice by decantation, and four or five times on the filter with small portions of hot water. The final washings should be practically free of chlorine.

The residue is ignited in a platinum dish, then treated with 25 cc. of acetic acid, and taken to dryness. This treatment is repeated and the residue taken up with a little hot water and filtered. The calcium fluoride is washed free of calcium acetate with small portions of water, remembering that $CaF_2$ is slightly soluble in water. The ignited residue is weighed as $CaF_2$.

$$CaF_2 \times 1.0757 = NaF.$$

**Sodium Sulphate.** — To the filtrate from calcium fluoride is added 10 cc. of hydrochloric acid and then a hot solution of barium chloride. The $BaSO_4$ is allowed to settle, filtered, washed, dried, ignited, and weighed as usual.

$$BaSO_4 \times 0.6086 = Na_2SO_4.$$

**Sodium Carbonate.** — Sodium carbonate is determined on a 5 gram sample by the usual method for carbon dioxide as described in the chapter on Carbon.

Approximate results may be obtained by adding a small excess of normal sulphuric acid to 5 grams of the fluoride in a platinum dish, boiling off the carbon dioxide, and titrating the excess of acid with normal caustic, using phenolphthalein indicator.

One cc. $N.H_2SO_4 = 0.053$ gram $Na_2CO_3$.
$H_2SO_4 \times 1.0816 = Na_2CO_3$.

**Sodium Chloride.** — Fifty cc. of the sample is titrated with N/10 $AgNO_3$ solution.

**Silica.** — This is probably present as sodium fluoride and silicate. One gram of the sample is dissolved in the least amount of water and a small excess of hydrofluoric acid added to convert the silicate to silico-fluoride, then an equal volume of alcohol. After allowing to stand for an hour, the precipitate is filtered, washed with 50% alcohol until free of acid and the filter and fluoride are placed in a beaker with 100 cc. of water, boiled and titrated with N/10 NaOH.

One cc. N/10 NaOH = 0.0015 gram $SiO_2$ or 0.0047 gram $Na_2SiF_6$.

**Volatile Matter and Moisture.** — One-gram sample is heated to dull redness to constant weight. Loss of weight is due to moisture and volatile products.

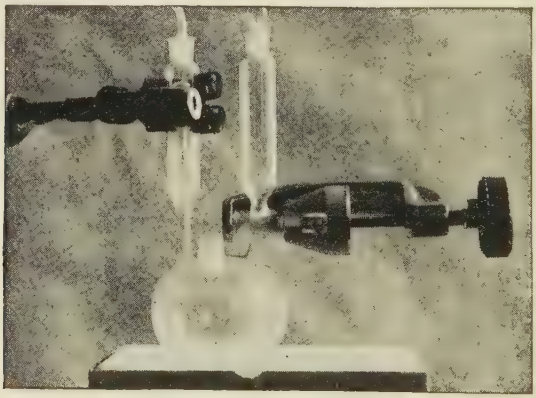


Fig. 78a — A Chessel Stop-cock Remover.
(Courtesy of Scharr & Co., Chicago, Ill.)

## GLUCINUM (BERYLLIUM)

**Gl, at.wt. 9.1; sp.gr. 1.85$^{20°}$; m.p.>960° C.; oxide, GlO**

### OCCURRENCE

Glucinum or Beryllium occurs combined in certain rare minerals.

*Minerals.*—The most important is *Beryl*, $Be_3Al_2(SiO_3)_6$. The color is usually some shade of green, but also blue, white, yellow, red or colorless; transparent to nearly opaque, vitreous lustre; brittle; harder than quartz, 7.5–8; gives a white streak. The crystals are hexagonal prisms, in length from mere threads to several feet, sometimes in large columnar masses.

### DETECTION

In the usual course of analysis glucinum will be precipitated by ammonia along with iron and aluminum hydroxides. Silica having been removed by evaporation to dryness of the acid solution of the substance, extraction of the residue with dilute hydrochloric acid and subsequent filtration, the members of the hydrogen sulphide group are precipitated from slightly acid solution by hydrogen sulphide. The filtrate is concentrated to about 30 cc., and about 2 grams of sodium peroxide are added to the cooled liquid, which is now heated to boiling and filtered. $Fe(OH)_3$ remains insoluble, if iron is present, while aluminum and glucinum dissolve. The filtrate is acidified with nitric acid, and ammonia then added in excess. If a precipitate forms, aluminum or glucinum or both are indicated. Glucinum hydroxide and aluminum hydroxide cannot be distinguished by appearance; the solubility of the former in sodium bicarbonate solution makes it possible to separate the two. The precipitate is dissolved in acid and the solution made almost neutral with ammonia. Solid sodium bicarbonate is added in sufficient amount to make the solution contain 10% of the reagent and the mixture heated to boiling, then filtered. Aluminum hydroxide remains on the filter paper and glucinum passes into the filtrate, in which it may be detected by diluting to ten volumes with water and boiling, whereupon glucinum hydroxide precipitates.

Glucinum hydroxide, $Gl(OH)_2$, is precipitated from neutral or acid solution by ammonia, insoluble in excess (distinction from $Al(OH)_3$). It is precipitated by sodium and potassium hydroxides, soluble in excess (separation from iron); if this solution is boiled $Gl(OH)_2$ is reprecipitated, $Al(OH)_3$ remains in solution. $Gl(OH)_2$ is soluble in an excess of ammonium carbonate, $Al(OH)_3$ is insoluble.

### Solution of the Sample

The oxide, GlO, is soluble in strong sulphuric acid. It is decomposed by fusion with potassium fluoride. The freshly precipitated hydroxide, $Gl(OH)_2$, is easily soluble in dilute acids, in alkalies and alkali carbonates and bicarbonates.

The methods of preparation and solution of the sample are the same as those described for the estimation of aluminum. For details of these procedures the analyst is referred to the chapter on this element.

**Removal of Silica and Members of the Hydrogen Sulphide Group.** — See procedure given under " Detection."

**Separation of Glucinum from Iron and Manganese.** — The acid solution is nearly neutralized with ammonia and then poured with constant stirring into an excess of a cold mixture of ammonium sulphide and carbonate. Iron and manganese are precipitated, whereas glucinum passes into the filtrate. (Zirconium and yttrium will be found with glucinum, if they are present in the material examined.)

**Separation from Zirconium and Yttrium.** — The filtrate obtained from the separation of iron and manganese is boiled for an hour, the precipitate is filtered and washed, then dissolved in dilute hydrochloric acid. To this solution is added an excess of sodium hydroxide, zirconium and yttrium are precipitated, whereas glucinum remains in solution. After filtering, glucinum may be precipitated by boiling the diluted filtrate.

**Separation from Aluminum, Chromium and Iron.** — The elements precipitated as hydroxides are ignited to oxides and fused with sodium carbonate for an hour or more. Upon leaching with water, aluminum and chromium dissolve, while iron and glucinum remain insoluble. The oxides of glucinum and iron may be separated by fusion with sodium acid sulphate, extracting with water and precipitating the iron with an excess of sodium hydroxide, glucinum remaining in solution.

**Separation of Glucinum from Aluminum.** — The hydroxides of aluminum and glucinum are precipitated with ammonia and the precipitate treated with an excess of ammonium carbonate. $Gl(OH)_2$ dissolves, whereas $Al(OH)_3$ remains insoluble. See Detection, also Gravimetric Method for Determination of Glucinum.

## GRAVIMETRIC DETERMINATION OF GLUCINUM

The procedure recommended by Parsons and Barnes depends upon the solubility of glucinum hydroxide in a 10% sodium bicarbonate solution, in the separation of this element from iron and aluminum hydroxide precipitate, with which it is commonly thrown out from solution. (Uranium, if present, also dissolves.)

**Procedure.** — Silica and the members of the hydrogen sulphide group having been removed by the usual methods (See Detection), hydrogen sulphide is expelled by boiling, nitric acid is added in sufficient amount to oxidize iron (the hydrochloric acid solution turns yellow) and ammonium hydroxide added in slight excess. The precipitated hydroxides are allowed to coagulate by heating to boiling[1] and, after settling a few minutes, filtered and washed with a 2% solution of ammonium acetate containing free ammonia.

**Separation from Iron and Aluminum Hydroxide.** — The precipitate is dissolved in hydrochloric acid, the solution oxidized with nitric acid or hydrogen peroxide (C.P.), if necessary, and the free acid then neutralized with ammonia. To the cold solution are added 10 grams of sodium bicarbonate for each 100 cc. of liquid. The mixture is heated to boiling and boiled for one minute, then cooled and filtered. The residue is washed with hot 10% solution of sodium bicarbonate. Iron and aluminum hydroxides remain on the filter and glucinum passes into the filtrate.

To recover occluded glucinum from the hydroxides of iron and aluminum, the precipitate is dissolved in a few drops of hydrochloric acid, and the precipitation repeated. It is advisable to repeat this a third time, adding the filtrates to the first portion containing the glucinum.

**Precipitation of Glucinum.** — The combined filtrates from the aluminum and iron hydroxides are acidified with strong hydrochloric acid, the beakers covered to prevent loss by spurting and the carbon dioxide completely removed by boiling. ($CO_2$ remaining in solution would form ammonium carbonate, on subsequent treatment with ammonia, which would dissolve glucinum.) A slight excess of ammonia is now added, the mixture again boiled and the precipitated glucinum hydroxide allowed to settle, then filtered and washed with a 2% solution of ammonium acetate containing free ammonia, until the chlorides are removed. After ignition the residue is weighed as glucinum oxide, GlO.

$$GlO \times 0.3626 = Gl.$$

[1] Prolonged boiling would cause the loss of too much $CO_2$, so that $Al(OH)_3$ would be apt to pass into solution. The evolution of $CO_2$ may be mistaken for boiling.

## GOLD

**Au, at.wt. 197.2; sp.gr. 19.33; m.p. 1063; b.p. 2530° C; oxides, $Au_2O$, $Au_2O_3$**

### OCCURRENCE

Gold is widely distributed in nature. It is found more commonly in igneous rocks of acid types, also in sedimentary and metamorphic rocks, in quartz veins, in placer deposits, alluvial sands, generally alloyed with silver and may contain copper, lead, iron, bismuth, etc. It occurs combined with tellurium and is frequently associated with pyrite, chalcopyrite, galena, sphalerite, arsenopyrite, tetradymite and other tellurium ores. It occurs in sea water. The important minerals are:

**Minerals.** — *Native Gold*, Au, a soft, malleable, opaque mineral with color and streak varying from golden yellow to yellowish white according to the silver content. It occurs in nuggets (In Australia two nuggets weighing 184 and 190 lbs. respectively, have been found), grains, scales or plates. Hardness 2.5–3.

*Gold Tellurides*, Calaverite, Sylvanite, Krennerite $(AuAg)Te_2$, Petzite $(AuAg)_2Te$, Nagyagite $Au_2Pb_{10}Sb_2Te_6S_{15}$.

The tellurides are granular massive, dull, often mixed with pyrite. Color silver white, yellow, steel gray or nearly black. Streak the same as the color. Calaverite is the most common.

### DETECTION

Because of the limited application and tediousness of wet methods, the detection of a small quantity (2 parts per million or less) of gold in a mineral or base metal is most positively carried out by furnace methods of assaying. Wet methods of detection of traces of gold can be applied only to solutions free of colored salts and elements precipitated by the reagents employed. As a rule, in the treatment of an unknown substance, advantage is taken of the solubility of most metals and their compounds, and insolubility of gold by one of the mineral acids.

Before the blowpipe on charcoal gold fuses to a bright yellow button, soluble in aqua regia, insoluble in the other mineral acids. Silver separates out as a white curd like precipitate. If the solution is evaporated to a viscous syrup and diluted with water, stannous chloride added and the solution warmed a purple precipitate forms, or a purple colored solution depending upon the amount of gold present "Purple of Cassius."

**Detection of Gold in Alloys.** — In metals or alloys which produce colorless solutions with dilute nitric acid, gold, in the absence of other insoluble matter, exhibits itself as a black or brownish residue which settles readily, and from which the liquid can be separated by careful decantation. If unassociated with metals of the platinum group, this residue will become yellowish brown on heating with strong nitric acid.

In copper, nickel and such alloys, which leave a residue of sulphur, carbon or silicious matter on treatment with dilute nitric acid, the solution is filtered through double ashless filters and the filter and residue incinerated in a porcelain crucible. The residue, which may require pulverizing, is digested for a few minutes with aqua regia, and the dilute, filtered solution evaporated to dryness by heating below 100° C. Just as soon as dry, the mass is moistened with the least quantity of hydrochloric acid and the *purple of Cassius test applied* to its water solution in a small volume. This test is made by adding a solution of stannous chloride, containing stannic chloride. In strongly acid and concentrated gold solutions a precipitate of brown gold is obtained. If the solution is but slightly acid and dilute, a reddish purple color is produced by colloidal gold and the stannic acid. The tint fades on standing. Addition of ammonia produces a red coloration.

This test applied to 1 part of gold in 600,000 of solution will impart a perceptible shade; to double this quantity, a mauve color. When gold is present in somewhat greater proportion a flocculent precipitate will form.

**Test for Gold in Minerals.** — From minerals, in which metal exists in unalloyed, or uncombined state, gold may be extracted by iodine in potassium iodide solution, or by chlorine or bromine water. All minerals containing sulphides should be roasted. In natural or roasted state the sample should be very finely pulverized, and usually yields the gold best if first digested with nitric acid and washed free of soluble salts. The sample in a flask is covered with bromine water, the flask closed with a plug and shaken frequently during a period of three or four hours. The purple of Cassius test is applied to the extract, removed by decantation after concentration.

If it is evident that base metals are present in the bromine water extract in quantity sufficient to mask the purple of Cassius test, hydrogen peroxide is added to the concentrated liquid, slightly alkaline with sodium or potassium hydroxide or carbonate. After boiling the solution until hydrogen peroxide is removed, precipitated hydroxides or carbonates are dissolved by hydrochloric acid. Gold in exceedingly small quantity exhibits itself as a light-brown residue on a fine filter. This indication should be confirmed by a purple of Cassius test on the aqua regia solution of the residue; the test carried out in the same manner as on the residue from a solution of a metal.

**Benzidine Acetate Tests.** — Maletesta and Nola make use of benzidine acetate (1 gram benzidine dissolved in 10 cc. acetic acid and 50 cc. water) as a reagent in the detection of gold and platinum in quite dilute solutions. Gold gives a blue coloration which gradually changes to violet. The coloration is green in the presence of free acetic acid, changing to blue with addition of benzidine in excess. Platinum gives a blue flocculent precipitate, the formation of which is promoted by heating. Free mineral acids have no influence on the gold and retard the platinum reaction only in the cold. Since ferric salts give a blue coloration, stable only in excess of benzidine, their absence must be assured before application of the test for the precious metals. The limit of sensitiveness of the test is 35 parts for gold and 125 parts for platinum per 10,000,000.

**Phenylhydrazine Acetate Test.** — E. Pozzi Escot adds phenylhydrazine acetate to a very dilute gold solution which contains an excess of an organic acid (formic or citric). A violet coloration, permanent for several hours, is imparted. The depth of color is proportional to the quantity when the gold is present in less amount than one part in 500,000.

*Dowsett's factory test of barren cyanide solutions* is capable of detecting variation in gold value of 1 cent per ton in solutions varying from one cent to about 15 cents per ton. To 500 cc. of the sample in a bottle with slight shoulder are added 10–15 cc. saturated sodium cyanide solution, 2 or 3 drops saturated lead nitrate solution and 1–2 grams 200-mesh fine zinc dust. The stoppered bottle is shaken violently until the precipitate settles rapidly. Inverting the bottle allows the precipitate to settle into a casserole. Clear liquid is removed by decantation. Zinc is dissolved by hydrochloric acid added drop by drop until reaction ceases. A few drops excess hydrochloric acid and 3–5 drops dilute nitric acid (sp. gr. 1.18) are added and the liquid concentrated to 1–2 cc. The solution is transferred to a $\frac{1}{2}$-in. diameter test-tube, about 1 cc. of stannous chloride reagent added and grade of cyanide solution estimated by the tint obtained after one or two minutes standing. 1/1000 oz. gold per ton of original cyanide solution gives a very slight coloration; 15/10000 a slight yellow; 1/500 a slight pinkish yellow; 3/1000 a strong pink; 1/250 the purple of Cassius. Too much nitric acid hinders the production and the presence of mercury causes modification of the color. No more lead nitrate should be used than is sufficient to produce a rapidly settling precipitate. The stannous chloride reagent is a water solution containing about $12\frac{1}{2}\%$ crystals and 10% concentrated hydrochloric acid.

### Solubility

Gold in massive form is practically insoluble in pure nitric, sulphuric or hydrochloric acids, but in the presence of oxidizing agents, is attacked appreciably by sulphuric, and actively by hydrochloric acid. Gold is found in minute quantity in the nitric acid solution of its alloys and in such as contain selenium, the amount may be a large part of the total present.

Gold is attacked energetically by aqua regia. Large amounts of gold are dissolved with requirement of least attention when the proportion of hydrochloric acid is several times that of the aqua regia formula, ($3HCl : 1HNO_3$).

Gold is dissolved by solutions of chlorine or bromine, by alkaline thiosulphates; in the presence of free oxygen by iodine in potassium iodide solution, by soluble cyanides, by fused potassium or sodium hydroxide; by fused potassium or sodium nitrate or sulphide. In a finely divided state, it is dissolved by a solution of potassium or sodium hydroxide.

Gold alloys quickly with molten lead. When in the form of bright, untarnished particles it alloys readily with mercury.

Gold is always weighed in metallic state, and is determined most accurately in the form of the mass obtained by dilute nitric acid treatment of the silver alloy resulting from the operation of cupellation in the method of assaying by furnace processes. On account of tediousness in making complete separation from associated metals, and of uncertainty in collection of the product in a form suitable for accurate weighing, direct precipitation methods are never used for the valuation of gold-bearing material, but may be applied to the estimation of gold in plating baths, the Wohlwill parting electrolyte and solutions of similar type.

## GRAVIMETRIC METHODS[1]

**Precipitation of Gold.** — From solutions of auric chloride, slightly acid with hydrochloric, freed of oxidizing agents by evaporation and displacement with hydrochloric acid, and containing but little of the salts of the alkalis or alkali earths, gold is separated from other than occluded platinum and palladium by precipitation with oxalic acid, ferrous sulphate, or hydrazine hydrochloride. The reactions are hastened by heat. When salts of the alkalis or earths are present, equally good separation and more complete precipitation can be obtained by addition of excess of sodium peroxide, boiling vigorously for a few minutes and then acidifying with hydrochloric acid. The precipitated metal is collected on an ashless filter paper, and after drying, weighed.

Gold precipitated from a very weak solution is in such fine form that it is not wholly retained by the finest paper.

### Wet Gold Assay of Minerals

A wet gold assay, suitable for prospector's use, is carried out by covering one assay ton (29.17 grams), of the finely pulverized natural or roasted ore, in a porcelain mortar, with 50 cc. of a solution of 2 parts of iodine and 4 parts potassium iodide in 100 cc. of water. Sulphide ores should be roasted and digested with nitric acid before treatment with the iodine solution. Similar treatment is advantageously applied to all ores. The ore is ground in contact with the iodine solution and additions of the halogen are made whenever the liquid becomes colorless. The solution is then allowed to stand at least an hour. To the filtrate and washings from the pulp, in a glass-stoppered bottle or flask, are added 5 grams of gold free mercury. The liquid is shaken vigorously with the mercury until clear. The mercury is then transferred to a small porcelain casserole, washed with clean water and dissolved by warming carefully with 10 cc. nitric acid. The gold mass is washed free of nitrate of mercury by decantation, dried and annealed by heating in a casserole over a Bunsen flame, and the metal weighed. Each milligram represents an ounce per ton. Results obtained by this method of assaying are usually more than 50 per cent of the actual gold content.

**Electrolytic Method.** — The gold content of a cyanide plating bath containing no potassium ferrocyanide may be estimated by electrolysis.

**Procedure.** — A measured quantity, 25 to 50 cc. in a tared platinum dish, is diluted to 1 cm. of the rim of the dish and using a carbon or platinum anode, electrolyzed for about three hours at a current density

[1] Gold is best determined by fire assay. See chapter on the subject by I. A. Palmer.

$ND_{100}$ = 0.067 amp. (0.0043 per square inch.) Completion of deposition is recognized by the lack of any deposit within fifteen minutes, on a platinum strip suspended on the rim of the dish. The dish plus gold deposit is washed, rinsed with alcohol, dried at 100° C., and when cold weighed.

The following is a summary of the conditions of deposition of gold in compact form as described by Classen. 3 grams potassium cyanide were added to a gold chloride solution containing 0.0545 grams of gold in 120 cc. This solution heated to about 55° C. when electrolyzed at a current density of $ND_{100}$ = 0.38 amp. (0.024 amp. per square inch) with a potential difference of 2.7–4.0 volts, deposited its gold content in one and a half hours. Time required for deposition is tripled if the electrolyte is at room temperature.

Gold is removed from the platinum electrode by warming with a solution of chromic anhydride in a saturated salt solution, or with a solution of potassium cyanide containing some oxidizing agent as hydrogen peroxide, sodium peroxide or alkali persulphate.

## VOLUMETRIC METHODS

These methods are applicable to the determination of the strength of chloride of gold solutions used in photography, electro gilding, and as electrolyte in the Wohlwill parting process.

**Preparation of the Sample.** — Nitric acid or nitrates in the solutions should be removed by repeated evaporations to syrup with addition of hydrochloric acid saturated with chlorine. Free chlorine or bromine should be removed by addition of ammonia to formation of permanent precipitate, then making the solution very slightly acid with hydrochloric acid and heating until the precipitate of fulminating gold dissolves. The gold solution should contain but little free hydrochloric acid, an excessive amount of which may be removed by ammonia.

### PERMANGANATE METHOD

Weak gold solutions should be concentrated whenever possible. The permanganate method, which is not applicable when the sample contains organic matter, depends upon the titration, after complete precipitation of gold, of the unoxidized portion of a measured quantity of an added reagent of a known gold precipitating value. The reagent may be ammonium or potassium oxalate, ferrous sulphate or ferrous ammonium sulphate in solutions varying from 5 to 25 milligrams gold precipitating value and is titrated with a permanganate solution of approximately equal oxidizing strength. One part of gold requires for precipitation 1.08 of ammonium oxalate, 1.40 of potassium oxalate, 4.22 of ferrous sulphate, 5.96 parts ferrous ammonium sulphate, each in crystalline form. The most satisfactory precipitations are made with the iron salts. The standard solution of either should contain about 0.1 per cent of sulphuric acid. One part of gold, in solution as auric chloride, has an oxidizing value equivalent to 0.4808 part of potassium permanganate.

The precipitating value of 0.2548 gram of dry Sorenson's sodium oxalate is 250 milligrams of gold, and by titrating a solution of this amount of oxalate in 250 cc. of water, acidulated with a few drops of sulphuric acid, the oxidizing value of the permanganate solution is obtained in terms of gold.

The value of the precipitating reagent and relative oxidizing value of the permanganate solution should be checked.

**Procedure.** — In carrying out the determination of a gold solution, a measured or weighed portion is freed of oxidizing agents, a measured amount of the standard precipitating reagent added in slight excess of the amount required to decolorize the solution, and digestion on a steam bath or hot plate continued until the gold settles out, leaving a clear liquid. A few drops of sulphuric acid may be then added and, without filtering, titration performed. The gold value of the quantity of reagent added, minus that found of the excess of reagent, is the gold content of the amount of the sample taken.

## COLORIMETRIC METHODS

Practical application of these methods is made in the estimation of gold in the liquors produced in the treatment of ores by the cyanide process.

### PRIESTER'S METHOD

By Prister's method a slight excess of copper solution is added to a 100 to 200-cc. portion of a cyanide solution in which the cyanide has been decomposed by boiling several minutes after acidifying with hydrochloric acid. Assurance of the presence of an excess of copper is made by spot test with a solution of potassium ferrocyanide.

The copper solution is made by boiling for ten minutes in contact with copper shavings, a solution of 1 part blue vitriol and 2 parts salt in 10 parts of water, and adding a little acetic acid on cooling. A few drops of a 1 to 2% sodium sulphide solution are added, the liquid boiled for five minutes, the precipitate allowed to settle, and liquid separated by decantation on to a filter. The precipitate in the beaker and on the filter is dissolved with $2\frac{1}{2}$ to 3 cc. of a 3 to 5% solution of potassium cyanide to which a few drops of potassium hydrate solution has been added.

Gold is precipitated from this cyanide solution (which may be turbid), by addition of 1 to 2 grams of zinc dust and warming to 100° F. for half an hour. Liquid is separated by decantation through a filter. The residue on the filter and in the beaker is first treated with hydrochloric acid to dissolve zinc, then with 10 cc. aqua regia, the reagent being passed several times through the filter. Stannous chloride solution is then added to the liquid diluted to 20 cc. Comparison of the coloration produced is made with that from a standard solution of gold treated in the same manner.

**Cassel's Method.** — By Cassel's method 0.5 gram potassium bromate is mixed with 10 to 50 cc. of the cyanide solution and concentrated sulphuric acid added gradually with constant agitation until reaction commences. When the reaction stops, saturated solution of stannous chloride is added dropwise until the liquid is just colorless. The tint produced is compared with that from a standard gold solution treated in the same manner.

**Moir's Method.** — By Moir's method a measured quantity of the cyanide solution is oxidized by addition of 1 to 2 grams of sodium peroxide and boiling. If sufficient sodium peroxide is present, the brown spot produced by addition of a few drops of lead acetate will immediately dissolve. The lead-aluminum couple formed by addition of aluminum powder precipitates gold which is filtered off. To the aqua regia solution of the precipitate a solution of stannous

chloride is added drop by drop until the liquid is dissolved. The purple of Cassius tint developed is compared with permanent standards composed of mixtures of solutions of copper sulphate and cobalt nitrate which have been adjusted to shades corresponding to those produced by known amounts of gold treated according to the method described.[1]

[1] This chapter was contributed by Mr. W. G. Derby, Research Chemist, Nichols Copper Company. — The Editor has taken the liberty to make a few deletions and additions, rearranging some of the material.

## HYDROGEN

**Properties.** — A colorless, odorless, tasteless gas; at.wt. 1.008; sp.gr. 0.07; b.p. −252° C; m.p. −259° C.

### OCCURRENCE

Hydrogen occurs free in small quantities in gases of volcanoes, and certain petroleum and gas wells; it occurs as a decomposition product in the decay of organic matter. It is found in traces in the atmosphere. It occurs chiefly combined with oxygen forming water.

Hydrogen occurs occluded or loosely combined in steel and alloys in which it may be determined as follows:

### DETERMINATION OF HYDROGEN IN STEEL

The method is based upon the oxidation of hydrogen liberated from steel by heat in presence of a current of oxygen. The water formed is absorbed and weighed.

**Procedure.** — Preliminary test. The apparatus is set up as shown in detail in Fig. 79. The heat is turned on and the oxygen gas

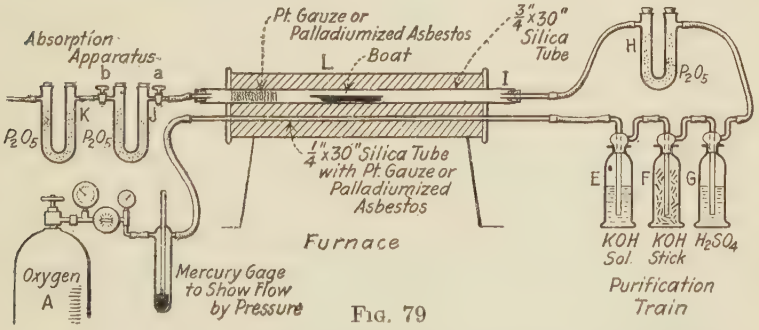



Fig. 79

passed through the silica tube I, heated to redness (850° C) at the rate of 100 cc. per minute, this rate having been established by a preliminary test noting the rate of bubbling through the acid in G and the pressure in C with the desired volume per minute. The gas is purified by passing through D, E, F, G and H, any hydrogen present being decomposed in the preheated tube D. Proceed now as follows:

Allow the gas to pass through the system for 5 to 10 minutes, disconnect the tube J after turning off the cocks "a" and "b" in

the order named. Place in the balance case for 5 minutes, then open and close " b " rapidly. The oxygen in J will be at atmospheric pressure and at the temperature in the balance. Now weigh. Replace the tube again in the train, open the cocks " a " and " b " and continue the flow of oxygen for another 10 minutes. If there is an increase in weight repeat the test a third time, noting the increase of weight during a 30 minute run. This is the blank that must be deducted from the regular run. It should not exceed 1 milligram.

**The Test** — Place in a clay boat previously ignited in a current of oxygen, or in a platinum boat containing ignited alundum powder, 10 to 30 grams of steel in as large pieces as possible (hydrogen is

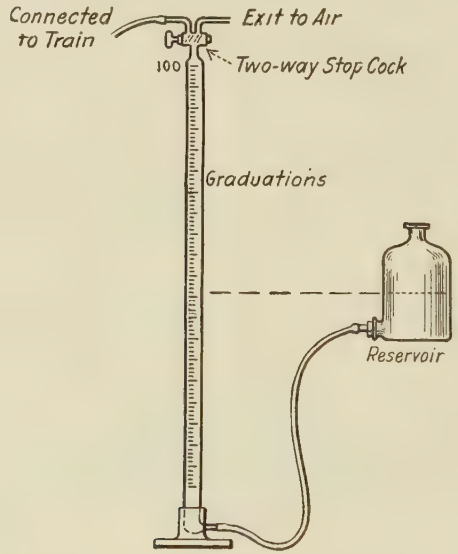



Fig. 80

liberated by drilling so that it is best to use the metal in strips or in a single piece). Insert the boat in the tube and quickly connect up the apparatus.

Turn on the oxygen at the rate of 100 cc. per minute and continue the flow for 30 minutes. Disconnect (after turning off cocks " a" and " b ") the absorption tube J. Place in balance case as before and equalize the pressure by opening the cock " b " for an instant. Weigh. The increase of weight, minus the blank, is due to the water formed. This weight multiplied by 0.111 gives the hydrogen of the sample.

Notes. The blank is derived from the oxidation of the rubber connections, and this should be determined and deducted from the regular run.

It is not necessary to burn all the metal to oxide to eliminate the hydrogen. A 30-minute run is sufficient.

The $P_2O_5$ is placed in the tubes interspersed with glass wool otherwise the tubes would pack, preventing the passage of the gas.

**Testing Gas Apparatus for Leaks.** — Connections between the parts of the gas apparatus, stop cocks, etc., should be tight to avoid intake or loss of gas, thus causing an error. The following simple method for testing for leaks is applicable to apparatus for the volumetric determination of gas as well as testing the tightness of combustion trains.

**Procedure.** — Close one end of the train. To the other attach a Hemple gas burette with two way stop cock and connected to a reservoir of water. Open the two way cock to the air and raise the reservoir until half of the gas in the tube is expelled. Now turn the cock to open a passage to the combustion train (or gas apparatus). Have the level of the water in the reservoir and the burette the same and note the exact reading. Now raise the reservoir about 10 inches, the gas will be under pressure. Lower the reservoir to its former position, levelling the water. If the level in the Hemple tube has risen an outward leak is indicated. See Fig. 80.

Now lower the reservoir to the table and after a few minutes raise to the first position. After levelling the water as before note whether the level has dropped in the Hemple. If so the apparatus leaks under reduced pressure.

## IODINE

**I, at.wt. 126.92; sp.gr. $4.948^{17°}$; m.p. 113.5°; b.p. 184.4° C.; acids, HI, HIO, $HIO_3$, $HIO_4$**

### OCCURRENCE

The element is found free in some mineral waters; combined as iodides and iodates in sea water; in ashes of sea plants; small quantities in a number of minerals, especially in Chili saltpeter as sodium iodate, hence in the mother liquor from the Chilian niter works from which iodine is principally produced. Sea-weed ash (drift kelp, Laminaria digitata and L. stenophylla) is an important source of iodine.

Free iodine, potassium iodide, iodoform, are the principal commercial products.

### DETECTION

**The element** may be recognized by its physical properties. It is a grayish black, crystalline solid, with metallic luster, brownish-red in thin layers. It vaporizes at ordinary temperatures with characteristic odor. Upon gently heating the element the vapor is evident, appearing a deep blue when unmixed with other gases, and violet when mixed with air. It colors the skin brown. Chemically it behaves very similarly to chlorine and bromine.

**Free iodine** colors water yellow to black, carbon disulphide violet, ether or chloroform a reddish color, cold starch solution blue.

Tannin interferes with the usual tests for iodine, unless ferric chloride is present.

**Iodide.** — The dry powder, heated with concentrated sulphuric acid, evolves violet fumes of iodine. Iodine is liberated from iodides by solutions of $As^5$, $Sb^5$, $Bi^5$, Cu″, Fe‴, $Cr^6$, $H_3Fe(CN)_6$, $HNO_2$, Cl, Br, $H_2O_2$, ozone.

Insoluble iodides may be transposed by treatment with $H_2S$, the filtered solution being tested for the halogen.

**Iodate.** — The acidulated solution is reduced by cold solution of $SO_2$, or $K_4Fe(CN)_6$, (acidulated with dilute $H_2SO_4$), or by $Cu_2Cl_2$, $H_3AsO_3$, $FeSO_4$, etc. An iodate in nitric acid may be detected by diluting the acid with water, adding starch solution, then hydrogen sulphide water, drop by drop, a blue zone forming in presence of the substance.

### SUGGESTION FOR STUDENTS

The beginner should study sections on "Preparation and Solution of the Sample," and "Separations." Determine the iodine in a sample of potassium iodide by the gravimetric silver iodide method and by the volumetric method of Fresenius, pages 292, 293.

## GRAVIMETRIC METHODS FOR DETERMINING IODINE

### Preparation and Solution of the Sample

In dissolving the substance it will be recalled that free iodine is soluble in alcohol, ether, chloroform, glycerole, benzole, carbon disulphide, solutions of soluble iodides. One hundred cc. of water at 11° C. is saturated with 0.0182 gram iodine, at 55° with 0.092 gram.

**Minerals.** — *Phosphates.* — The substance is decomposed by digestion with 1 : 1 sulphuric acid in a flask through which a current of air passes to sweep out the iodine vapor into a solution of potassium hydroxide, the sample being boiled until all the iodine vapors have been driven into the caustic. Iodates are converted to iodides by reduction with sulphurous acid.

With the iodine content below 0.02%, a 50 to 100-gram sample should be taken.

**Iodides** of silver, copper (cuprous), mercury (mercurous), and lead are insoluble, also TlI, $PdI_2$. Iodides of other metals are soluble; those of bismuth, tin, and antimony require a little acid to hold them in solution.

**Iodates** of silver, barium, lead, mercury, bismuth, tin, iron, chromium require more than 500 parts of water at 15° C. to hold them in solution. Iodates of copper, aluminum, cobalt, nickel, manganese, zinc, calcium, strontium, magnesium, sodium, and potassium are more soluble. One hundred cc. of cold water dissolves 0.00385 gram $AgIO_3$ and 0.000035 gram AgI at ordinary temperatures.

**Free Iodine (Commercial Crystals).** — Iodine is best brought into solution in a strong solution of potassium iodide according to the procedure described for standardization of sodium thiosulphate under Volumetric Methods. The iodine is now best determined volumetrically by titration with standard thiosulphate or arsenic.

**Separation of Iodine from the Heavy Metals.** — The heavy metals are precipitated as carbonates by boiling with solutions of alkali carbonates, the soluble alkali iodide being formed.

Iodine is liberated from combination by nitrous acid.

Silver iodide may be decomposed by warming with metallic zinc and sulphuric acid.

### PRECIPITATION AS SILVER IODIDE

The procedure is practically the same as that described for determining chlorine.

Silver nitrate solution is added to the iodide solution, slightly acidified with nitric acid. The precipitate is filtered into a weighed Gooch crucible, then washed, dried, gently ignited, and weighed as silver iodide.

$$AgI \times 0.5406 = I \text{ or } \times 0.7071 = KI.$$

### DETERMINATION OF IODINE AS PALLADOUS IODIDE

This method is applicable for the direct determination of iodine in iodides in presence of other halogens.

The method of isolation of iodine as the palladous salt has been given under Separations. The salt dried at 100° C. is weighed as $PdI_2$.

$$PdI_2 \times 0.704 = I.$$

$PdI_2$ ignited in a current of hydrogen is changed to metallic palladium.

$$Pd \times 2.379 = I.$$

## VOLUMETRIC METHODS

### DETERMINATION OF HYDRIODIC ACID IN SOLUBLE IODIDES

Free hydriodic acid cannot be determined by the usual alkalimetric methods for acids. The procedure for its estimation, free [1] or combined as a soluble salt, depends upon the liberation of iodine and its titration with standard sodium thiosulphate, in a neutral or slightly acid solution; or by means of standard arsenious acid, in presence of an excess of sodium bicarbonate in a neutral solution. The following equations represent the reactions that take place:

**I. Thiosulphate.** $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$.

**II. Arsenite.** $Na_3AsO_3 + I_2 + H_2O = Na_3AsO_4 + 2HI$.

The free acid formed in the second reaction is neutralized and the reversible reaction thus prevented:

$$HI + NaHCO_3 = NaI + H_2O + CO_2.$$

The presence of a free alkali is not permissible, as the hydroxyl ion would react with iodine to form iodide, hypoiodite and finally iodate, hence sodium or potassium carbonates cannot be used. Alkali bicarbonates, however, do not react with iodine.

**Standard Solutions. — Tenth Normal Sodium Thiosulphate.** — From the reaction above it is evident that 1 gram molecule of thiosulphate is equivalent to 1 atom iodine = 1 atom hydrogen, hence a tenth normal solution is equal to one-tenth the molecular weight of the salt per liter, e.g., 24.82 grams $Na_2S_2O_3.5H_2O$; generally a slight excess is taken — 25 grams of the crystallized salt. It is advisable to make up 5 to 10 liters of the solution, taking 125 to 250 grams sodium thiosulphate crystals and making up to necessary volume with distilled water, boiled free of $CO_2$. The solution is allowed to stand a week to ten days, and then standardized against pure, resublimed iodine.

About 0.5 gram of the purified iodine is placed in a weighing bottle containing a known amount of saturated potassium iodide solution (2 to 3 grams of KI free from $KIO_3$ dissolved in about 0.5 cc. of $H_2O$), the increased weight of the bottle, due to the iodine, being noted. The bottle and iodine are placed in a beaker containing about 200 cc. of 1% potassium iodide solution (1 gram KI per 100 cc.), the stopper removed with a glass fork and the iodine titrated with the thiosulphate to be standardized.

**Calculation.** — The weight of the iodine taken, divided by the cc. thiosulphate required, gives the value of 1 cc. of the reagent; this result divided by 0.012692 gives the normality factor.

Note. The thiosulphate solution may be standardized against iodine, which has been liberated from potassium iodide in presence of hydrochloric acid

[1] Convert to alkali salt.

by a known amount of standard potassium bi-iodate, a salt which may be obtained exceedingly pure.

$$KIO_3.HIO_3 + 10KI + 11HCl = 11KCl + 6H_2O + 6I_2.$$

A tenth normal solution contains 3.2496 grams of the pure salt per liter. (One cc. of this will liberate 0.012692 gram of iodine from potassium iodide.) The purity of the salt should be established by standardizing against thiosulphate, which has been freshly tested against pure resublimed iodine.

About 5 grams of potassium iodide (free from iodate) are dissolved in the least amount of water that is necessary to effect solution, and 10 cc. of dilute hydrochloric acid (1:2) are added, and then 50 cc. of the standard bi-iodate solution. The solution is diluted to about 250 cc. and the liberated iodine titrated with the thiosulphate reagent; 50 cc. will be required if the reagents are exactly tenth normal.

**Tenth Normal Arsenite.** — From the second reaction above it is evident that $As_2O_3$ is equivalent to $2I_2$, e.g., to 4H, hence $\frac{1}{4}$ the gram molecular weight of arsenious oxide per liter will give a normal solution: $198 \div 4 = 49.5$.

4.95 grams of pure arsenious oxide is dissolved in a little 20% sodium hydroxide solution, the excess of the alkali is neutralized with dilute sulphuric acid, using phenolphthalein indicator, the solution being just decolorized. Five hundred cc. of distilled water containing about 25 grams of sodium bicarbonate are added. If a pink color develops, this is destroyed with a few drops of weak sulphuric acid. The solution is now made to volume, 1000 cc. The reagent is standardized against a measured amount of pure iodine. The oxide may be dissolved directly in sodium bicarbonate solution.

Note. Commercial arsenious oxide is purified by dissolving in hot hydrochloric acid, filtering the hot saturated solution, cooling, decanting off the mother liquor, washing the deposited oxide with water, drying and finally subliming.

**Starch Solution.** — Five grams of soluble starch are dissolved in cold water, the solution poured into 2 liters of hot water and boiled for a few minutes. The reagent is kept in a glass-stoppered bottle.

The addition of a few cc. of 5% NaOH, then heating to boiling and filtering will preserve the starch.

## DECOMPOSITION OF THE IODIDE BY FERRIC SALTS

The method takes advantage of the following reaction:

$$Fe(SO_4)_3 + 2KI = K_2SO_4 + I_2 + 2FeSO_4.$$

The procedure enables a separation from bromides, as these are not acted upon by ferric salts.

**Procedure.** — To the iodide in a distillation flask is added an excess of ferric ammonium alum, the solution acidified with sulphuric acid, then heated to boiling, and the iodine distilled into a solution of potassium iodide. The free iodine in the distillate is titrated with

standard thiosulphate, or by arsenious acid in presence of an excess of sodium bicarbonate.

The reagent is added from a burette until the titrated solution becomes a pale yellow color. About 5 cc. of starch solution are now added and the titration continued until the blue color of the starch fades and the solution becomes colorless.

One cc. of tenth normal reagent = 0.012692 gram iodine, equivalent to 0.012793 gram HI, or 0.016602 gram KI.

### DECOMPOSITION OF THE IODIDE WITH NITROUS ACID (FRESENIUS)

Nitrous acid reacts with an iodide as follows:

$$2HNO_2 + 2HI = 2NO + 2H_2O + I_2.$$

Since neither hydrochloric nor hydrobromic acids are attacked by nitrous acid, the method is applicable to determining iodine in presence of chlorine and bromine; hence is useful for determining small amounts of iodine in mineral waters containing comparatively large amounts of the other halogens.

**Nitrous Acid.** — The reagent is prepared by passing the gas into strong sulphuric acid until saturated.

FIG. 81

**Procedure.** — The neutral or slightly alkaline solution of the iodide is placed in a glass-stoppered separatory funnel, Fig. 81, and slightly acidified with dilute sulphuric acid. A little freshly distilled colorless carbon disulphide (or chloroform) is added, then 10 drops of nitrous acid reagent. The mixture is well shaken, the disulphide allowed to settle, drawn off from the supernatant solution and saved for analysis. The liquor in the funnel is again extracted with a fresh portion of disulphide and if it becomes discolored it is drawn off and added to the first extract. If the extracted aqueous solution appears yellow, it must be again treated with additional carbon disulphide until all the iodine has been removed (e.g., until additional $CS_2$ is no longer colored when shaken with the solution). The combined extracts are washed with three or four portions of water, then transferred to the filter and again washed until free from acid. A hole is made in the filter and the disulphide allowed to run into a small beaker and the filter washed down with about 5 cc. of water. Three cc. of 5% sodium bicarbonate are added and the iodine titrated with N/20 or N/50 standard thiosulphate, the reagent being added until the reddish-violet carbon disulphide becomes colorless.

The sodium thiosulphate used is standardized against a known amount of pure potassium iodide treated in the manner described above.

One cc. N/20 $Na_2S_2O_3$ = .00635 gram I, 1 cc. N/50 $Na_2S_2O_3$ = .002538 gram I.

### VOLHARD'S METHOD

The solution of the iodide, placed in a glass-stoppered flask, is diluted to about 300 cc. and standard silver solution added with vigorous agitation until the yellow precipitate collects and the supernatant solution is no longer cloudy — a slight excess of silver solution is added and the excess titrated with standard potassium thiocyanate as in case of the determination of chlorine, using ferric alum as indicator. See chapter on chlorine.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Determination of Iodine in Mineral Waters and Brines

The following procedure is given by W. F. Baughman and W. W. Skinner.

Take such a quantity of the brine or water as will contain not more than 0.1 g. iodine as iodide or more than 10 g. total salts. Adjust the volume to 100 cc. to 150 cc. and boil it with a sufficient amount of sodium hydroxide and sodium carbonate to precipitate the calcium and magnesium. Filter off the precipitate and wash with hot water. Introduce the filtrate into an Erlenmeyer flask, adjust the volume to about 100 cc., neutralize with dilute sulphuric acid, and add 1 cc. of a solution of sodium hydroxide (4 g. per 100 cc.). Heat to boiling, add an excess of potassium permanganate, continue the heating until the precipitate begins to coagulate, and then allow to cool. Add sufficient alcohol to cause the permanganate color to disappear and allow the precipitate to settle on the steam bath. Filter and wash with hot water. After cooling, add one or two grams of potassium iodide, acidify with hydrochloric acid, and titrate with standard thiosulphate. The number of cc. required, divided by 6, represents the number of cc. required by the iodine in the sample.

## IRIDIUM

**Element, Iridium. Ir. at.wt. 193.10; sp.gr. 22.3; m.p. 2350° C.?**
**oxides, $IrO_2$, $Ir_2O_3$**

Iridium is a grayish white, brittle metal. Hardness 6–7. Infusible and insoluble in all acids. Attacked by chlorine gas. Substances in which iridium is determined are: platinum scrap, jewelers' sweeps, contact points, ores. Iridium is weighed as the metal.

### OCCURRENCE

In platinum ores and in gold sands. Generally alloyed with platinum.

### DETECTION

Iridium is found associated with platinum. The element is insoluble in all acids, including aqua regia. Chlorine is the best reagent. This forms the chlorides of iridium and yields compounds with other chlorides as $K_2IrCl_6$, which is insoluble. If the element is heated in a stream of chlorine in the presence of potassium chloride there forms a salt, $K_2IrCl_6$, which is sparingly soluble and is used in the separation of iridium.

The oxide, $Ir_2O_3$ is formed when $K_2IrCl_6$ is mixed with sodium carbonate and gently fused at a dull red heat.

$$2K_2IrCl_6 + 4Na_2CO_3 = Ir_2O_3 + 8NaCl + 4KCl + 4CO_2 + O.$$

The fusion is dissolved in water containing ammonium chloride; the residue is separated from the extract by filtration and ignited to expel the ammonium chloride. It is now treated with dilute acid in order to remove the small quantity of alkali. A bluish-black powder is thus obtained which begins to decompose when heated above 800 degrees, and at temperatures somewhat above 1000 degrees is completely broken up into oxygen and the metal.

The dioxide, $IO_2$, is a black powder obtained by heating the hydroxide in a current of carbon dioxide. It is insoluble in acids.

**Caustic Alkalies** produce in a boiling solution a dark-blue precipitate of $Ir(OH)_4$ insoluble in all acids except HCl.

**Potassium chloride** forms the double salt of $K_2IrCl_6$, which is black and is difficultly soluble in water.

**Ammonium chloride** precipitates black $(NH_4)_2IrCl_6$, which is difficultly soluble in water.

**Hydrogen sulphide** precipitates black $Ir_2S_3$, soluble in $(NH_4)_2S$.

**Metallic zinc** precipitates from an acid solution black metallic iridium.

**Formic acid and sulphurous acid** precipitate black metallic iridium from hot solutions.

**Lead acetate** gives a gray-brown precipitate.

**Potassium and sodium carbonate** give a black precipitate and the solution being highly oxidized on cooling is a nice blue or violet blue.

**When an iridium salt is heated with concentrated sulphuric acid** and a small amount of silver nitrate is added, there forms a gorgeous blue color by which 1/1000 of a milligram of iridium may be detected. With the presence of HCl and an addition of $NH_4Cl$ and $NH_4NO_3$, a rose-red color forms. The reaction is likewise very sharp.

## METHODS FOR DETERMINING IRIDIUM

### Preparation and Solution of the Sample

Platinum scrap and contact points, etc., containing iridium dissolve with difficulty in aqua regia, depending on the amount of iridium present. The alloy is dissolved more quickly if it is rolled or hammered to a very thin sheet or ribbon. The alloy of platinum and iridium with an iridium content up to 10% dissolves in aqua regia slowly; an alloy of iridium content of 15% dissolves in aqua regia very slowly and the aqua regia will likely have to be replenished from time to time. An alloy of 25% iridium is practically insoluble in aqua regia. The filings from sweeps, etc., can be dissolved by aqua regia the same as the scrap. After expelling the $HNO_3$ the platinum and the iridium are precipitated together with $NH_4Cl$ as $(NH_4)_2PtCl_6$ and $(NH_4)_2IrCl_6$. When the precipitate is ignited to metal it forms an alloy of platinum and iridium. The iridium imparts a pinkish to a scarlet color to the salt.

If the iridium content is too high to be dissolved in aqua regia the metal can be mixed with NaCl, heated to a dull red heat in a porcelain or silica tube, and moist chlorine passed over the mixture. The iridium will be in the form of a chloride which dissolves in water. After filtering the solution and evaporating with HCl, the iridium as well as the platinum is precipitated with $NH_4Cl$ or $H_2S$. This is a convenient way on a larger scale to dissolve osmiridium in ores.

When the iridium is contaminated with a large amount of impurities, it may be reduced from the solution with zinc, and the impurities dissolved by $HNO_3$ and dilute aqua regia; the residue is washed and dried as iridium.

Clean osmiridium grains are also brought into solution by a fusion of $KNO_3$, $NaNO_3$ or $KClO_3$ and NaOH or KOH, leaving the iridium as $Ir_2O_3$.

**Separation of Iridium from Platinum.** — See Separation of Pt from Ir.

If the platinum and iridium are alloyed with at least ten times their weight of silver and the alloy dissolved in $HNO_3$, the silver and the platinum dissolve, leaving the iridium insoluble. After washing the residue, treat with a small amount of dilute aqua regia to dissolve any platinum that may be present.

*Separation from Osmium.* — Osmium is removed by distillation.

## GRAVIMETRIC METHODS FOR THE DETERMINATION OF IRIDIUM

### 1. By Reduction with Zinc

The solution of iridium or iridium and platinum is treated with C.P. granulated zinc and 5% free HCl. The iridium and the platinum are precipitated as fine black metal. The black metal is washed free from impurities and the platinum insoluble portion is dried, ignited, reduced with hydrogen and weighed as metallic iridium.

### 2. By Igniting the Salt $(NH_4)_2IrCl_6$

The percentage of iridium in the salt may be judged fairly well by the color, by comparing with standard iridio-platinum salts. The salt is filtered, washed with alcohol and carefully ignited and weighed as iridio-platinum sponge metal. The percentage of iridium in the sample can be calculated from the weight of the iridium obtained. The two metals are now digested at about 40 or 50° C. in aqua regia, diluted with about five times its weight of water — the aqua regia being renewed until it is no longer colored. The residue is pure iridium.

### 3. By Obtaining it as a Residue

The iridium and the platinum, etc., are alloyed with at least ten times their weight of silver and the alloy dissolved in $HNO_3$. The residue will be a small amount of platinum, gold, if any present, and iridium. Add a small amount of dilute aqua regia, which will dissolve the gold and the rest of the platinum, leaving the iridium as a black residue. This is filtered, washed and ignited and weighed as metallic iridium.

One part of the iridium material is alloyed with eight parts of lead. This is packed in a graphite capsule, and the whole embedded in charcoal in an ordinary assay crucible. Heat to a high temperature in a furnace for several hours. When the crucible and contents are cold, remove the lead and clean well. Treat the lead with dilute $HNO_3$, thus removing the lead and leaving the iridium as the residue. Wash thoroughly and treat the residue with dilute aqua regia, which leaves the residue as pure iridium. If other metals of the platinum group are present, see separations under those metals.[1]

[1] This chapter was compiled by Mr. R. E. Hickman, Consulting Chemist, J. Bishop & Co. Platinum Works.

## IRON

**Fe, at.wt. 55.84; sp.gr. 7.85–7.88; m.p. pure 1530°, wrought 1600°, white pig 1075°, gray pig 1275°, steel 1375°; b.p. 2450° C.; oxides FeO, $Fe_2O_3$, $Fe_3O_4$**

### OCCURRENCE

Iron occurs so widely diffused in nature that its determination is necessary in practically all complete analysis of ores, rocks, minerals and especially in the evaluation of ores of iron, such as the oxides — red and brown hematite, black magnetite; the sulphides iron pyrites and pyrrhotite; the carbonates such as spatic iron ore, combined with clay in clay ironstone with bituminous material as "black band." Iron is determined in cinders and in iron ore briquettes from burned iron pyrites, by-products of sulphuric acid. It is looked for as an impurity in a large number of commercial salts and in the mineral acids.

**Minerals.** — Ferric oxide with varying amounts of water forms the substances known as hematite, göthite, limonite, yellow ochre, bog iron ore. Among the very large number of minerals of iron known we will take up a few of the more important:

*Native Iron* — Fe, found sparingly in eruptive rocks usually in small grains; masses from size of a walnut to thousands of pounds occur in basalt; most meteorites are either alloys of iron and nickel or contain these. The mineral is opaque, steel gray to iron black substance, tough and malleable, magnetic, soluble in acids giving a yellow colored solution when dissolved in hydrochloric acid containing a little nitric acid. Streak is a metallic gray; hardness 4–5.

*Pyrrhotite*, Magnetic Pyrites $Fe_nS_{n+1}$ = $Fe_6S_7$ to $Fe_{11}S_{12}$, a massive bronze yellow to red metallic mineral; magnetic; opaque; brittle; grayish black streak; hardness 3.5–4.5. Distinguished from pyrite, bornite and niccolite by its magnetic property.

*Pyrite*, Iron Pyrites, Fool's Gold, a brass colored, metallic, brittle, opaque mineral, frequently with cubic or other isometric crystalline form or variable; streak greenish-black; hardness 6–6.5.

*Marcasite*, White Iron Pyrites, $FeS_2$ distinguished from pyrite by crystalline form (orthorhombic), cleavage, and slighter effect of oxidizing agents.

*Hematite*, Specular Iron, Red Iron Ore, $Fe_2O_3$, black, dark red to cherry-red, opaque, brittle (unless micaceous), mineral with metallic to dull lustre; streak brownish-red to cherry-red; hardness 5.5–6.5.

*Magnetite*, Lodestone, Magnetic Iron Ore, $Fe_2O_3.FeO$, a black, opaque, brittle, metallic to submetallic mineral which gives a black

streak, magnetic or strongly attracted by magnet. Loose to compact coarse or fine grained masses. Insoluble in nitric acid, but dissolves in hydrochloric.

*Limonite*, Brown Hematite, Bog-Ore, $Fe_2(OH)_6.Fe_2O_3$, frequently quite impure from sand clay, etc., a loose, porous earthy ochre of brown to yellow color, opaque, dull lustre, or compact varieties with silky lustre; streak yellowish-brown; hardness 5–5.5.

*Siderite*, Spatic Ore, $FeCO_3$, a gray, yellow, brown or black, opaque to translucent, brittle mineral with vitreous to pearly lustre, occurring in granular masses or masses with rhombohedral cleavage, hexagonal crystals. Varieties — Blackband, Clay Ironstone, Spherosiderite. Hardness 3.5–4.

Other Minerals of Iron Chalcopyrite, $CuFeS_2$; Arsenopyrite, FeAsS; Ilmenite, $FeTiO_3$; Chromite, $FeO.Cr_2O_3$; Göthite, $Fe_2O_3.H_2O$; Almandite, $Fe_3Al_2(SiO_4)_3$; Andradite, $Ca_3Fe_2(SiO_4)_3$; Columbite, Tantalite, $(Fe.Mn)(Nb.Ta)_2O_6$; Wolframite, $(Fe.Mn)WO_4$; Hypersthene, Acmite, Anthophyllite, Glaucophane, Riebeckite, Crocidolite, Greenalite, Ilvaite, Staurolite, Triphylite, Copiapite, etc.

## DETECTION

The material is dissolved in sulphuric, hydrochloric or hydrochloric nitric acids. It is not necessary to effect complete solution to detect iron in the substance.

**Ferric Iron.** — The yellow to red color in rocks, minerals, and soils is generally due to the presence of iron.

**Hydrochloric acid** solutions of iron as ferric chloride are colored yellow.

**Potassium or ammonium sulphocyanate** produces a red color with solutions containing ferric iron. Nitric acid and chloric acid also produce a red color with potassium or ammonium sulphocyanate. This color, however, is destroyed by heat, which is not the case with the iron compound. The red color of ferric iron with the cyanate is destroyed by mercuric chloride and by phosphates, borates, certain organic acids, and their salts, e.g., acetic, oxalic, tartaric, citric, racemic, malic, succinic, etc.

**Potassium ferrocyanide, $K_4Fe(CN)_6$**, produces a deep blue color with ferric salts.

**Salicylic acid** added to the solution of a ferric salt containing no free mineral acid gives a violet color. Useful for detecting iron in alum and similar products.

**Ferrous Iron. — Potassium Ferricyanide, $K_3Fe(CN)_6$**, gives a blue color with solutions of ferrous salts.

**Distinction between Ferrous and Ferric Salts.**

**KCNS** gives a red color with Fe‴ and no color with Fe″.

**$K_3Fe(CN)_6$** gives a blue color with Fe″ and a brown or green with Fe‴.

**$NH_4OH$, NaOH** or **KOH** precipitates red $Fe(OH)_3$ with $Fe'''$ and white, $Fe(OH)_2$ with $Fe''$ turning green in presence of air due to oxidation. The green product is a hydrate of $Fe_3O_4$. The white precipitate can be obtained in the absence of air, or by using sulphur dioxide gas to take up the oxygen in the solution.

**Sodium peroxide** produces a reddish-brown precipitate of $Fe(OH)_3$ with either ferrous or ferric salt solutions, the former being oxidized to the higher valence by the peroxide. Chromium and aluminum remain in solution, if present in the sample.

## SUGGESTION FOR STUDENTS

Read the sections on "Preparation and Solution of the Sample" and "Separations." Read the introductory paragraphs to the volumetric procedures. Determine iron in a sample by the Dichromate and by the Permanganate methods, using the methods recommended for students.

## METHODS FOR DETERMINING IRON

### Preparation and Solution of the Sample

The material should be carefully sampled and quartered down according to the general procedure for sampling. Ores should be ground to pass an 80 mesh sieve. In analysis of metals, both the coarse and fine drillings are taken.

The following facts regarding solubility should be remembered: The *element* is soluble in hydrochloric acid and in dilute sulphuric acid, forming ferrous salts with liberation of hydrogen. It is insoluble in concentrated, cold sulphuric acid, but is attacked by the hot acid, forming ferric sulphate with liberation of $SO_2$. Moderately dilute, hot nitric acid forms ferric nitrate and nitrous oxide; the cold acid gives ferrous nitrate and ammonium nitrate or nitrous oxide or hydrogen. Cold, concentrated nitric acid forms "passive iron," which remains insoluble in the acid. The *oxides of iron* are readily soluble in hydrochloric acid, if not too strongly ignited, but upon strong ignition the higher oxides dissolve with extreme difficulty. They are readily soluble, however, by fusion with acid potassium sulphate followed by an acid extraction. *Silicates* are best dissolved by hot hydrochloric acid containing a few drops of hydrofluoric acid or by fusion with sodium and potassium carbonates, followed by hot hydrochloric acid.

**Soluble Iron Salts.** — Water solutions are acidified with HCl or $H_2SO_4$, so as to contain about 3% of free acid.

**Ores.** — The samples should be pulverized to pass an 80 to 100 mesh sieve.

**Sulphides, Ores Containing Organic Matter.** — One to 5-gram samples should be roasted in a porcelain crucible over a Bunsen flame for about half an hour, until oxidized. The oxide is now dissolved as directed in the following procedure.

**Oxides, Including Red and Brown Hematites, Magnetic Iron Ore, Spatose Iron Ore, Roasted Pyrites, and Iron Ore Briquettes.** — One to 5 grams of the ore, placed in a 400 cc. beaker, is dissolved by adding twenty times its weight of strong hydrochloric acid with a few drops of 5% stannous chloride solution. Addition of 4 or 5 drops of HF is advantageous if small amounts of silica are present. The solution is covered with a watch-glass and heated to 80 or 90° C. until solution is complete. Addition of more stannous chloride may be necessary, as this greatly assists solution. An excess sufficient to completely decolorize the solution necessitates reoxidation with hydrogen peroxide, hence should be avoided. If a colored residue remains, it should be filtered off, ignited and fused with a mixture of $Na_2CO_3$ and $K_2CO_3$ in a platinum crucible. The fusion dissolved in dilute HCl is added to the main filtrate.

Note. The ore placed in a porcelain boat in a red-hot combustion tube may be reduced with hydrogen (taking precaution first to sweep out oxygen

with $CO_2$) and after cooling in an atmosphere of hydrogen the reduced iron may be dissolved in acid and titrated.

**Iron Silicates.** — One to 5 grams of the material, placed in a deep platinum crucible, is treated with ten times its weight of 60% HF and 3 to 4 drops of conc. $H_2SO_4$. The mixture is evaporated to near dryness on the steam bath and taken up with dilute sulphuric acid or hydrochloric acid. The latter acid is the best solvent for iron.

**Fusion with Potassium Bisulphate.** — The sample is mixed with ten times its weight of the powdered bisulphate and 2–3 cc. of concentrated sulphuric acid added. A porcelain or silica dish will do for this fusion. The fusion should be made over a moderate flame and cooled as soon as the molten liquid becomes clear. Complete expulsion of $SO_3$ should be avoided. It may be necessary to cool and add more concentrated sulphuric acid to effect solution. Iron and alumina completely dissolve, but silica remains undissolved. The melt is best cooled by pouring it on a large platinum lid.

**Fusion with Carbonates of Sodium and Potassium.** — The residues insoluble in hydrochloric acid are fused with 5 parts by weight of the fusion mixture ($Na_2CO_3 + K_2CO_3$) in a platinum crucible. The Méker blast will be necessary. When the effervescence has ceased and the melt has become clear, the crucible is removed from the flame, a platinum wire inserted and the melt cooled. Upon gently reheating, the fuse may be readily removed by the wire in a convenient form for solution in dilute hydrochloric acid.

The bisulphate fusion is recommended for fusion of residues high in iron and alumina. It is an excellent solvent for ignited oxides of these elements. The carbonate fusions are adapted to residues containing an appreciable amount of silica.

**Iron and steel** are best dissolved in hydrochloric acid with a few drops of nitric acid. The iron hydroxide should be precipitated or the solution taken to dryness to expel the nitric acid followed by resolution in dilute hydrochloric acid or sulphuric acid.

## METHODS FOR ISOLATING IRON

**General Procedure.** — In the usual course of analysis silica is removed by evaporating the acid solution to dryness, taking up with water and filtering. Mercury, lead, bismuth, copper, cadmium, arsenic, antimony, tin, molybdenum and other elements precipitated from an acid solution as sulphides are removed as such by filtration and iron, after oxidation to the ferric state, is precipitated as $Fe(OH)_3$. In the majority of cases it may now be determined with accuracy by titration.

**Special Cases.** — Separation of iron, where necessary in special cases, may be accomplished according to details given in the chapters dealing with the elements from which a separation is desired.

**Ether Method for Removing Iron from a Solution.** — Ferric chloride dissolved in HCl (sp.gr. 1.1) is more soluble in ether than in this acid. Advantage is taken of this fact when it is desired to remove a greater portion of the iron in determining copper, nickel, cobalt, chromium, vanadium and sulphur (as $H_2SO_4$) in steel. The hydrochloric acid solution of iron, etc., is evaporated to a syrupy consistency and then taken up with HCl (sp.gr. 1.1) and transferred by means of more of the acid to a separatory funnel. The cold acid solution is now extracted several times by shaking with ether, each time allowing the ether carrying the iron to separate before drawing off the lower layer for re-extraction. Three extractions are generally sufficient for removing the iron.

## GRAVIMETRIC METHODS FOR THE DETERMINATION OF IRON

The gravimetric determination of iron may be made from solutions practically free from other metals. A number of elements such as phosphorus, arsenic, molybdenum, tungsten, vanadium, and the like, form fairly stable compounds with iron in neutral or slightly alkaline solutions, whereas others, such as lead, copper, nickel, cobalt, sodium, and potassium may be occluded in the ferric hydrate precipitate and are removed only with considerable difficulty. Aluminum, chromium, and several of the rare earths are precipitated with iron, if present. These facts taken into consideration, the volumetric methods are generally preferred as being more rapid and trustworthy.

### DETERMINATION OF IRON AS $Fe_2O_3$

Iron is precipitated as the hydroxide and ignited to the oxide, $Fe_2O_3$.

**Reactions.** $FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl.$
$2Fe(OH)_3 + \text{heat} = Fe_2O_3 + 3H_2O.$

**Procedure.** — One gram, sample, or a larger amount of material if the iron content is low, is brought into solution with hydrochloric acid, aqua regia, or by fusion with potassium carbonate or potassium acid sulphate, as the case may require. Silica is filtered off and the acid solution treated with $H_2S$ if members of that group are present. The filtrate is boiled to expel $H_2S$ and the iron oxidized to ferric condition by boiling with 5 cc. of concentrated nitric acid.

**Absence of Aluminum and Chromium.** — About 1 gram of ammonium chloride salt or its equivalent in solution is added, the volume made to about 200 cc. and ammonium hydroxide added in slight excess to precipitate $Fe(OH)_3$. The solution is boiled for about five minutes, and filtered.

**If Aluminum and Chromium are Present.** — In place of ammonium hydroxide powdered sodium peroxide is added in small portions until the precipitate first formed clears, the solution being cold and nearly neutral. It is diluted to about 300 cc. and boiled ten to fifteen minutes to precipitate the iron. Aluminum and chromium are in solution. (Mn will precipitate with Fe, if present.) The precipitate is filtered onto a rapid filter and washed with hot water.

**Second Precipitation.** — In either case the precipitate is dissolved with the least amount of hot dilute hydrochloric acid and the paper washed free of iron. A few cc. of 10% ammonium chloride solution are added and the hydroxide of iron precipitated by adding an excess of ammonium hydroxide, the volume of the solution being about 200 cc. Washing the precipitate by decantation is advisable. Three such

washings with 50 cc. of water, followed by two or three on the filter paper, will remove all impurities.

**Ignition.** — The precipitate is ignited wet over a low flame, gradually increasing the heat. Blasting is not recommended, as the magnetic oxide of iron, $Fe_3O_4$, will form with high heating. The oxide heated gently appears a reddish-brown. Higher heat gives the black oxide, $Fe_3O_4$. Twenty minutes' ignition at red heat is sufficient.

The crucible and residue, cooled in a desiccator, are weighed and the iron oxide determined.

Factors. $Fe_2O_3 \times 0.6994 = Fe$. $Fe_2O_3 \times 0.8998 = FeO$.

## PRECIPITATION OF IRON WITH "CUPFERRON," AMINO NITROSOPHENYL-HYDROXYLAMINE[1]

By this procedure iron may be precipitated directly in acid solution in presence of a number of elements. Mercury, lead, bismuth, tin, and silver may be partially precipitated. Copper precipitates with iron, but may be easily removed by dissolving it out with ammonia. The method is especially adapted for separation of iron from aluminum, nickel, cobalt, chromium, cadmium, and zinc.

**Procedure.** — The solution containing the iron is made up to 100 cc. and 20 cc. of concentrated hydrochloric acid added. To this cool solution (room temperature) Baudisch's reagent, cupferron, is slowly added with constant stirring, until no further precipitation of iron takes place, and crystals of the reagent appear. The iron precipitate is a reddish-brown. Copper gives a grayish-white flocculent compound. An excess of the reagent equal to one-fifth of the volume of the solution is now added, the precipitate allowed to settle for about fifteen minutes, then poured into a filter paper and washed, first with 2N.HCl, followed by water, then with ammonia and finally with water. The drained precipitate is slowly ignited in a porcelain or platinum crucible and the residue weighed as $Fe_2O_3$.

$$Fe_2O_3 \times 0.6994 = Fe.$$

Notes. Baudisch's reagent, amino nitrosophenyl-hydroxylamine (cupferron), is made by dissolving 6 grams of the salt in water and diluting to 100 cc. The reagent keeps for a week if protected from the light. It decomposes in the light, forming nitrobenzine. Turbid solutions should be filtered.

The precipitates of copper or iron are but slowly attacked by twice normal hydrochloric acid in the cold, but decomposed by hot acid, hence the solution and reagent should be cold.

Cold, dilute potassium carbonate solution, or ammonium hydroxide, have no action on the iron precipitate; the copper compound dissolves readily in ammonia. Alkaline hydroxide causes rapid decomposition.

The precipitation is best made in comparatively strong acid solutions (HCl, $H_2SO_4$, or acetic acid).

[1] O. Baudisch, Chem. Ztg., 33, 1298, 1905. Ibid., 35, 913, 1911. O. Baudisch and V. L. King, Jour. Ind. Eng. Chem., 3, 627, 1911.

## VOLUMETRIC DETERMINATION OF IRON IN ORES AND METALLURGICAL PRODUCTS

**General Considerations.** — Two general procedures are commonly employed in the determination of iron.

*A*. Oxidation of ferrous to ferric condition by standard oxidizing agents.

*B*. Reduction of ferric iron to ferrous condition.

The sample is dissolved as directed under Preparation and Solution of the Sample.

### DETERMINATION OF IRON BY OXIDATION METHODS

Some modification of either the dichromate or permanganate method is commonly employed in the determination of iron by oxidation. To accomplish this quantitatively, the iron must be reduced to its ferrous condition. This may be accomplished by any of the following methods:

**1. Reduction by Hydrogen Sulphide.** — During the course of a complete analysis of an ore, $H_2S$ is passed into the acid solution to precipitate the members of that group (Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Pt, Au, Se, etc.). The filtrate contains iron in the reduced condition suitable for titration with either dichromate or permanganate, the excess of $H_2S$ having been boiled off. If the expulsion of $H_2S$ is conducted in an Erlenmeyer flask there is little chance for reoxidation of the iron during the boiling. Reduction by $H_2S$ is very effective and is frequently advisable. This is the case when titanium is present, since this is not reduced by $H_2S$, but by methods given below. Arsenic, antimony, copper, and platinum, which, if present would interfere, are removed by this treatment.

**Reaction.** $2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$

**2. Reduction with Stannous Chloride.** — $SnCl_2$ solution acts readily in a hydrochloric acid solution of the ore; the reduction of the iron is easily noted by the disappearance of the yellow color. The excess of the reagent is oxidized to $SnCl_4$ by addition of $HgCl_2$.

**Reactions.**
1. $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$
2. Excess $SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl$ precipitated.

An excess of $SnCl_2$ is advisable, but a large excess is to be avoided, as a secondary reaction is apt to take place, as follows: $2SnCl_2 + 2HgCl_2 = 2SnCl_4 + 2Hg$. This reaction is indicated by the darkening of the solution upon the addition of $HgCl_2$. Precipitation of metallic mercury would vitiate results. The solution should be cooled before

addition of mercuric chloride. About 15–20 cc. of saturated mercuric chloride, $HgCl_2$, solution should be sufficient.

**3. Reduction by a Metal such as Test Lead, Zinc, Magnesium, Cadmium, or Aluminum, in Presence of Either Hydrochloric Acid or Sulphuric Acid.** — The former acid is preferred with the dichromate titration, and the latter with the permanganate. Two methods of metallic reduction are in common use — reduction by means of test lead, and reduction with amalgamated zinc by means of the Jones reductor.

(*a*) **Reduction with Test Lead.** — By this method copper is precipitated from solution and small amounts of arsenic and antimony expelled. Sufficient test lead is added to the acid ferric solution to completely cover the bottom of the beaker. The solution is covered and boiled vigorously until the yellow color has completely disappeared, and the solution is colorless. The reduced iron solution, cooled, is decanted into a 600 cc. beaker, the remaining iron washed out from the lead mat by several decantations with water; two or three 50 cc. portions of water should be sufficient; the washings are added to the first portion. If the solution becomes slightly colored, a few drops of stannous chloride, $SnCl_2$, solution are added, followed by 10 cc. mercuric chloride, $HgCl_2$, solution. The sample is now ready for titration.

(*b*) **Reduction with Zinc, Using the Jones Reductor.** — The acid solution of iron, preferably sulphuric acid, is passed through a column of amalgamated zinc. The hydrogen evolved in presence of the zinc reduces the ferric iron to ferrous condition. The procedure is described in detail under the Permanganate Method for Determination of Iron, page 317. Titanium if present will also be reduced.

**4. Reduction with Sulphurous Acid, Sodium Sulphite or Metabisulphite.** — $SO_2$ gas is passed into a neutral solution of iron, since iron is not reduced readily in an acid solution by this method. The excess $SO_2$ is expelled by acidifying the solution and boiling.

**5. Reduction with Potassium Iodide.** — The iodide is added and the liberated iodine is expelled by heat.

*In the solution of the ore with stannous chloride and hydrochloric acid, if an excess of the former has been accidentally added, it will be necessary to oxidize the iron before reduction. This may be accomplished by addition of hydrogen peroxide until the yellow color of ferric chloride appears; the excess* $H_2O_2$ *may be removed by boiling (or by addition of* $KMnO_4$ *solution). The iron may now be reduced by one of the above methods.*

**Reagents used in standard oxidation of the reduced solutions.** Two reagents are generally used, potassium dichromate and potassium permanganate. Either of these reagents give excellent results.

**Potassium dichromate** acting as an oxidizing agent has the following advantages: — The salt may be obtained in exceedingly pure form so that the gram molecular weight can be taken into the exact calculation for making up the solution, i.e. a N/10 solution contains $\frac{1}{6}$ of

294.2 grams of the pure salt. (See Introduction, also see discussion in the chapter on Reagents) The salt remains unaltered in the air and the solution kept in a stoppered bottle remains constant on standing. The salt has no water of crystallization which causes uncertainty in the composition of so many compounds. It is not affected by hydrochloric acid which is so often used as a solvent. It does not act on rubber and may be used in burettes with rubber tips (Mohr burette). Its disadvantage is that it requires an outside indicator (See Introduction). It does not give up its oxygen to many substances, which are oxidized by potassium permanganate. The reagent is used almost entirely in the determination of iron.

**Potassium Permanganate.** — Although the salt may be produced with high grade of purity from other substances, a small amount of manganese dioxide is generally present, which slowly decomposes the reagent solutions, producing more dioxide. Hence it is necessary to filter the reagent after allowing it to stand for a few hours, to remove this dioxide, the filtering being conducted through asbestos. The reagent has the advantage of being its own indicator, no spot plate tests with an outside indicator being necessary as in case of the dichromate, the reagent becoming decolorized by a reducing agent. Permanganate attacks rubber so that a Mohr rubber tipped burette cannot be used in titrations with $KMnO_4$ solutions.

## VOLUMETRIC DETERMINATION OF IRON BY OXIDATION WITH POTASSIUM DICHROMATE

**Principle.** — This method depends upon the quantitative oxidation of ferrous salts in cold acid solution (HCl or $H_2SO_4$) to ferric condition by potassium dichromate, the following reaction taking place:

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2CrCl_3 + 2KCl + 7H_2O.$$

Potassium ferricyanide is used as an outside indicator. This reagent produces a blue compound with ferrous salts and a yellowish-brown with ferric. The chromic salt formed by the reaction with iron colors the solution green.

### Reagents Required

**Standard Potassium Dichromate.** — When oxygen reacts with ferrous salts, the following reaction takes place:

$$6FeCl_2 + 6HCl + 3O = 6FeCl_3 + 3H_2O.$$

Since $K_2Cr_2O_7 \simeq K_2O \cdot Cr_2O_3 \cdot 3O$

Comparing this reaction with that of dichromate, it is evident that a normal solution of dichromate contains one-sixth of the molecular weight of $K_2Cr_2O_7$ per liter, namely, 49.033 grams. For general use it is convenient to have two strengths of this solution, N/5 for ores high in iron and N/10 for products containing smaller amounts.

Note. Make up the reagent as follows if it is desired to have the dichromate of such strength that 1 cc. is equivalent to 1% iron on the basis of 0.5 gram sample. Since 1% on 0.5 gram is 0.005 gram Fe and since Fe $= \frac{1}{6}$ $K_2Cr_2O_7$ or 55.84 g. Fe = 49.033 g. $K_2Cr_2O_7$, therefore 0.005 g. Fe = (49.033 ÷ 55.84) × 0.005 = 0.0042 g. $K_2Cr_2O_7$ per cc. or 4.202 g. per liter. With the above strength of reagent a 50 cc. burette is convenient.

**Standardization.** — For N/5 solution 9.807 grams of the recrystallized dehydrated salt are dissolved and made up to one liter; N/10 potassium dichromate contains 4.903 grams of the pure salt per liter. It is advisable to allow the solution to stand a few hours before standardization.

Methods for the standardization of potassium dichromate are given in the chapter of Preparation of Reagents. Some laboratories prefer to use a standard ore of iron in place of the standards given in the above chapter. For those desiring to use a standard ore, it is advisable to start with the Sibley iron ore furnished by the U.S. Bureau of Standards, Washington, D.C., as the ultimate standard. Other ores uniform in iron may be standardized against the Sibley ore and used as standards. The ore in question contains 69.20% of Fe (1914). For accurate work it is desirable to use a chamber burette with graduations from 75 to 90 cc. in tenths and from 90 to 100 in

twentieths of a cc. A titration of 90 to 100 cc. of the dichromate would require 0.9 to 1.1 grams of iron for a fifth normal solution and half this amount for a tenth normal solution of dichromate. In the first case 1.4 grams of Sibley iron ore should be taken and for N/10 0.7 gram of the ore. The ore is best dissolved in strong HCl, adding a few drops of stannous chloride solution and heating just below boiling. In case of an ore or iron ore briquette, containing silica in an appreciable amount, a carbonate fusion of the residue may be necessary. Reduction and titration of the ore is done exactly as prescribed under Procedure below.

The equivalent iron in the ore divided by the cc. titration required for complete oxidation gives the value in terms of grams per cc., e.g., 1.4 grams of ore containing 69.2% of Fe required a titration of 95 cc. of $K_2Cr_2O_7$ solution, then,

$$1 \text{ cc.} = \frac{(69.2 \times 1.4)}{100} \div 95 = 0.0102 \text{ gram Fe.}$$

**Stannous Chloride.** — Sixty grams of the crystallized salt dissolved in 600 cc. of strong HCl and made up to one liter. The solution should be kept well stoppered.

**Mercuric Chloride.** — Saturated solution of $HgCl_2$ (60 to 100 grams per liter).

**Potassium Ferricyanide, $K_3Fe(CN)_6$.** The salt should be free of ferrocyanide, as this produces a blue color with ferric salts. A crystal the size of a pinhead is dissolved in 50 cc. of water. The solution should be made up fresh for each set of determinations.

**Apparatus. — Chamber burette.**—This should read from 75 to 90 cc. in tenths and from 90 to 100 cc. in twentieths of a cc., the chamber being 75 cc.

**Test-Plate.** — The usual porcelain test-plate with depressions may be replaced by a very simple and efficient test-sheet made by dipping a white sheet of paper in paraffin. The indicator does not cling to this surface, the drops assuming a spherical form, which renders the detection of the end-point more delicate.

### Procedure

**Iron Ores.** — If a chamber burette is used, as is described under apparatus, together with a fifth normal dichromate solution, the amount of sample taken should be such that the actual iron present would weigh between 0.9 to 1.1 grams. This weight can be estimated by dividing 95 by the approximate percentage of iron present, e.g., for 50% Fe ore take $\frac{95}{50} = 1.9$ grams; 95% iron material would require 1 gram, whereas 20% Fe ore would require 4.75 grams.

If a 50 cc. burette is used with an 0.1 N.$K_2Cr_2O_7$ reagent, a half

gram sample is taken. See note under Standard Potassium Dichromate.

For samples containing less than 20% of Fe it is advisable to use N/10 $K_2Cr_2O_7$ solution.

The sample should be finely ground (80 mesh).

**Solution.** — The hydrochloric acid method for solution of the oxidized ore with subsequent carbonate fusion of the residue is recommended as being suitable for iron ores, briquettes, and materials high in iron.

**Reduction.** — $H_2S$ reduction is recommended in ores containing arsenic or titanium. $SnCl_2$ in very slight excess, followed by mercuric chloride, $HgCl_2$, gives excellent results in absence of other reducible salts of elements, Cu, As, etc.

**Test Lead.** — The easy manipulation and efficiency of this method of reduction makes it applicable for a large variety of conditions. The acid solution preferably, HCl, is diluted to about 150 to 200 cc., containing 15 to 20 cc. of concentrated hydrochloric acid (sp.gr. 1.19). Sufficient test lead is added to cover the bottom of a No. 4 beaker. The solution covered is boiled vigorously until it becomes colorless. Copper, if present, is precipitated, as well as platinum, and small amounts of arsenic and antimony eliminated from the solution during the reduction of the iron. The cooled solution is poured into a 600 cc. beaker and the mat of lead remaining in the No. 4 beaker washed free of iron, two or three 50 cc. washings being sufficient. The main solution and washings are combined for titration. If the solution is slightly colored, due to reoxidation of iron, a few drops of stannous chloride solution are added to reduce it, followed by an excess of $HgCl_2$ solution, 20 to 25 cc., and allowed to stand five minutes.

**Titration.** — Dilute the solution to about 500 cc. and titrate with standard potassium dichromate, adding the reagent to within five or six cc. of that required (determined by the first sample tested) rapidly and then cautiously making outside spot tests with the potassium ferricyanide indicator as directed in the first procedure. As a precaution in the first run it is advisable to reserve a portion of the solution to be titrated to avoid overrunning the end-point, this reserve being added when the end-point of the first portion has been reached.

If the standard chamber burette is used, titrate with N/5 dichromate, 1 cc. of which is equivalent to 0.011168 g. Fe.

For student use 50 cc. burettes are generally preferred, using N/10 reagent, 1 cc. of which is equivalent to 0.005584 g. Fe.

Notes. If $SnCl_2$ solution has been used for reduction of the iron, it is necessary to add the $HgCl_2$ rapidly to a cold solution, as slow addition to a warm solution is apt to precipitate metallic mercury.

In case an excess of dichromate has been added in the titration, as often occurs, back titration may be made with ferrous ammonium sulphate $(NH_4)_2SO_4.FeSO_4.6H_2O$. N/10 solution of this reagent may be prepared by dissolving 9.81 grams of the clear crystals in about 100 cc. of water, adding 5 cc. of concentrated $H_2SO_4$ and making to 250 cc. The solution should be standard-

ized against the dichromate solution to get the equivalent values, by running the dichromate directly into the ferrous solution.

The ferricyanide indicator should be made up fresh each time it is required.

Large amounts of manganese in the iron solution titrated cause a brown coloration, which masks the end-point. Nickel and cobalt, present in large amounts are objectionable for the same reason. This interference may be overcome by using very dilute acid solutions of ferricyanide indicator, so that the insoluble ferricyanide of these metals will not form.

## OPTIONAL DICHROMATE METHOD

To become familiar with the dichromate method it is advisable to titrate a known amount of standard ferrous ammonium sulphate with the standard potassium dichromate using the spot test on the tile as directed in the first procedure. For academic purposes 50 cc. burettes are convenient with N/10 dichromate reagent, or a solution 1 cc. of which is equivalent to 1% Fe on 0.5 gram sample taken. Following this preliminary practice determine the iron in a sample of iron ore as follows:

**Reagents.** — These are the same as described in the first method.

**Solution of the Ore.** — Weigh two samples of finely ground ore (60–80 mesh, no grit should be evident when tested with the fingers) taking about 0.5 gram and heating in a porcelain crucible to dull redness to destroy organic matter. Transfer each to a beaker and treat with about 3 cc. stannous chloride and 20 cc. of hydrochloric acid, covering beaker and heat until the dark particles have disappeared, adding more acid, if necessary. Do not evaporate to dryness. Dilute with a few cc. of water. The residue should be white otherwise it must be digested longer to effect decomposition of the iron. If the solution is colorless, due to an excess of stannous chloride, add very cautiously, drop by drop, a N/10 solution of potassium permanganate, until a faint yellow color appears. (Insoluble residue colored, see note.)

**Reduction of the Iron.** — To the hot solution containing the iron (diluted to about 50 cc.) add the stannous chloride drop by drop until the yellow color just disappears and then a drop or two in excess. Cool rapidly by placing the beaker in cold water, and when cold add about 15 cc. of 5% mercuric chloride. A white silky precipitate will form. (If gray or dark, metallic mercury has been produced by the presence of too much stannous chloride and the run must be repeated.)

**The Spot Test.** — A series of drops of very dilute solution of potassium ferricyanide, (a crystal about the size of a pin head in 200 cc. of water. The ferricyanide should be free of ferrocyanide otherwise the end-point will be uncertain since the ferrocyanide gives a blue color with ferric salts) are placed on a white tile (spot plate) and the tests made by placing a drop of the titrated sample in a drop

of the reagent on the test plate. As long as a blue color is produced ferrous iron is present, the end-point appears colorless or faint yellow.

$$1 \text{ cc. } N/10 K_2Cr_2O_7 = 0.005584 \text{ g. Fe.}$$

NOTE. Insoluble residue. — If the acid treatment does not effect complete decomposition of the dark material, decant the solution (diluted to about 50 cc.) through a filter, wash the residue several times with distilled water. Determine iron in the filtrate and washings by the procedure described above — meantime, fuse the residue in a platinum crucible with about 6 times its weight of sodium and potassium carbonates, dissolve the fusion in dilute HCl, adding a little $HNO_3$ to oxidize the iron (beaker covered). Precipitate the iron from this solution with $NH_4OH$, filter off $Fe(OH)_3$. Dissolve in HCl and follow above procedure, adding the per cent of iron obtained to the percentage obtained from the acid extract.

## POTASSIUM PERMANGANATE METHOD FOR DETERMINATION OF IRON

**Introduction.** — The method depends upon the quantitative oxidation of ferrous salts to the ferric condition when potassium permanganate is added to their cold solution, the following reaction taking place:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Hydrochloric acid in presence of iron salts has a secondary reaction upon the permanganate, e.g.,

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 10Cl.$$

This reaction may be prevented by addition of large amounts of zinc or manganous sulphates together with an excess of phosphoric acid or by diluting largely with water the solution titrated. Hydrochloric acid may be expelled by adding sulphuric acid and taking to fumes. If the solution is sufficiently dilute HCl does not interfere with the permanganate titration. See optional method following. The solution is diluted and reduced with zinc and titrated as directed.

Since potassium permanganate enters into reaction with acid solutions of antimony, tin, platinum, copper and mercury, when present in their lower state of oxidation, (also with manganese in neutral solutions) and with $SO_2$, $H_2S$, $N_2O$, ferrocyanides and with most soluble organic bodies, these must be absent from the iron solution titrated.

Potassium permanganate produces an intense pink color in solution, so that it acts as its own indicator.

**Solutions Required.** — **Standard Permanganate Solutions.** — As in case of potassium dichromate, it is convenient to have two standard solutions, N/5 and N/10.

From the reaction given above it is evident that 2 $KMnO_4$ are equivalent to 5 oxygens, e.g., $2KMnO_4 = K_2O + 2MnO + 5O$, hence a normal solution would contain one-fifth of the molecular weight of $KMnO_4$ = 31.6 grams of the pure salt. Hence a N/5 solution would contain 6.32 grams per liter and a N/10 solution 3.16 grams.

Since commercial potassium permanganate is seldom pure, it is necessary to determine its exact value by standardization. This is commonly accomplished by any of the following methods:

(*a*) By a standard electrolytic iron solution.

(*b*) By ferrous salt solution, e.g., $(NH_4)_2SO_4.FeSO_4.6H_2O$.

(*c*) By oxalic acid or an oxalate.

The methods for standardization of potassium permanganate are given in the chapter on Preparation of Reagents. Reference is made to this chapter for details of standardization.

The reduction of the sample is best effected by means of metallic zinc, by either adding this to the sample in a flask, preferably with a

Bunsen valve (permitting the escape of the hydrogen but preventing an intake of air) or by passing the solution, under examination, through a column of zinc. This latter procedure is recommended where a large number of determinations are made. For occasional determinations of irons some prefer reduction by adding zinc to the solution in a covered beaker, any excess of zinc being filtered off on a cotton wad loosely placed in a funnel. See optional method following.

**Amount of the Sample.** — If a factor weight 0.559 gram of the sample is taken then 1 cc. of a N/10 solution of permanganate will equal 1 %.

Note. If 2.83 grams of pure $KMnO_4$ are dissolved and made to 1000 cc., 1 cc. will be equivalent to 1 % Fe per 0.5 gram sample, since 55.84 g. Fe requires 31.6 g. $KMnO_4$ for oxidation and .005 g. Fe requires (31.6 ÷ 55.84).005 = .00283 g. $KMnO_4$ per cc. or 2.86 g. per liter. Absolute reliance cannot be placed on the purity of the permanganate so that the percentage value is approximate only.

## PROCEDURE FOR THE DETERMINATION OF IRON BY THE JONES REDUCTOR

**Preparation of Sample.** — Such an *amount* of the sample is taken that the iron content is between two- and three-tenths of a gram (0.2 to 0.3 gram). If hydrochloric acid has been required to effect solution, or hydrochloric acid and nitric acid (25 cc. : 1 cc.), as in case of iron and steel, 4 to 5 cc. of conc. sulphuric are added, and the solution evaporated to small bulk on the steam bath and to $SO_3$ fumes to remove hydrochloric acid. The iron is taken up with about 50 cc. of dilute sulphuric acid, 1 : 4, heating if necessary, and filtering if an insoluble residue remains. In a solution containing 10 cc. HCl diluted to 700 cc. the HCl does not interfere in the permanganate titration. See optional method following.

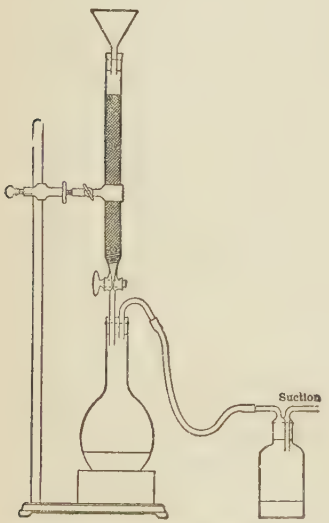


FIG. 82. — Jones Reductor.

**Preparation of the Reductor.** — Cleaning out the apparatus. See Fig. 82. The stop-cock of the reductor is closed, a heavy-walled flask or bottle is put into position at the bottom, and 50 cc. of dilute sulphuric acid poured into the funnel. The cock is opened and the acid allowed to flow slowly through the zinc in the tube, applying a gentle suction. Before the acid has drained out of the funnel, 50 cc. of water are added, followed by 50 cc. more of dilute sulphuric acid and 50 cc. of water in turn. The stop-cock is turned off before the water has drained completely from the funnel so that the zinc is always covered by a solution of acid or water. This precaution should be observed in all determinations with the Jones reductor to prevent the inflow of air into the column of zinc. The contents of the flask being emptied and the flask replaced, the apparatus is ready for the determination of the blank.

**Determination of the Blank.** — Fifty cc. of dilute sulphuric acid, 1 : 4, are passed through the reductor, followed by 250 cc. of distilled water, according to the directions given above. The acid solution in the flask is then titrated with N/10 $KMnO_4$ solution. If more than 3 or 4 drops of the permanganate are required, the operation must be repeated until the blank titration does not exceed this amount. The final blank obtained should be deducted from the regular determinations for iron. The end-point of the titration is a faint pink, persisting for one minute.

**Reduction and Titration of the Iron Solution.** — The sample is diluted to 200 cc., and, when cold, is run into the funnel, the stop-cock opened and the solution drawn slowly through the column of zinc into the flask, about four minutes being required for 200 cc. of solution. Before the funnel has completely drained, rinsings of the vessel which contained the sample are added; two 50 cc. portions are sufficient, followed by about 50 cc. of water. The stop-cock is closed before the solutions have completely drained from the funnel.

**Titration.** — The flask is removed and tenth normal solution of permanganate added until a faint pink color, persisting one minute, is obtained. The blank is deducted from the cc. reading of the burette.

Cc. $KMnO_4$, thus found multiplied by the value of the reagent in terms of N/10 = true value of N/10 $KMnO_4$ required to oxidize the reduced iron.

One cc. N/10 $KMnO_4$ = .005584 gram Fe; or .007984 gram $Fe_2O_3$.

## OPTIONAL METHOD FOR IRON IN ORES

The procedure recommended by A. H. Low for students, has been found to give excellent results, the following outline is his own. For further details reference is made to his IX edition of Technical Methods of Ore Analysis.

1. **Solution of the Sample.** — 0.5 gram of ore. 8-oz flask. With oxidized ores add 10–15 cc. of HCl and warm gently until the iron oxide is dissolved; then if sulphides are also present add 5 cc. of $HNO_3$ to decompose them also. With straight sulphides use 10 cc. of HCl and 5 cc. of $HNO_3$. When decomposition is complete add 5 cc. of $H_2SO_4$ and boil over a free flame nearly to dryness.

2. **Reduction.** — After cooling, add 30 cc. water, 10 cc. HCl and 6 grams of 20 mesh granulated zinc. Not necessary to get salts into solution. Now add 3 cc. of a 4% copper sulphate solution. Allow to stand until the action has become feeble.

3. Add 50 cc. of cold water and then 10 cc. of strong $H_2SO_4$ and allow to stand until the zinc is nearly all dissolved.

4. **Filtration from Insoluble Gangue and Excess Zinc.** — Prepare a filter by placing a rather thick wad of absorbent cotton in a funnel and wetting it into place. Place a battery jar, or a liter beaker containing about an inch of cold water, under the funnel. Have the beaker marked at the 700 cc. point.

5. When the zinc in the flask has nearly all dissolved, filter the liquid through the absorbent cotton and wash out the flask at least 10 times with cold water, pouring through the filter. Use the wash bottle reversed to save time, and use enough water for each wash to completely cover the absorbent cotton. Allow to drain between washes. Continue the washing until the filtrate reaches the 700 cc. mark on the beaker.

6. **Titration of the Sample.** — Titrate at once with standard permanganate to a very faint pink tinge and take reading.

7. A blank should previously be run on the zinc to determine any correction (usually due to a little iron) necessary. Deduct this correction from the above reading.

8. Multiply the cc. of permanganate used by the factor for iron.

9. **Standardization of Permanganate.** — Standard Permanganate. About 2.83 grams per liter. Standardize on oxalic acid of Sorensen's salt, as described in text book. Multiply the oxalic acid value by 0.8855 to obtain the Fe value, or the Sorensen's salt value by 0.8332. 1 cc. of permanganate should equal about 0.005 gram fe., or about 1% on the basis of 0.5 gram of ore taken for assay.

## STANNOUS CHLORIDE METHOD FOR DETERMINATION OF FERRIC IRON

The procedure is based upon the reduction of the yellow ferric chloride to the colorless ferrous salt by stannous chloride, the following reaction taking place:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

The method is of value in estimating the quantity of ferric iron in presence of ferrous, where the two forms are to be determined. In order to obtain the total iron the ferrous is oxidized by adding a few crystals of potassium chlorate and taking to dryness to expel chlorine, and then titrated with stannous chloride.

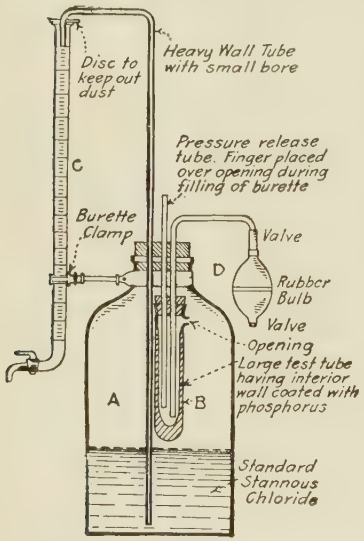



Fig. 83. — Apparatus for Stannous Chloride Titration of Iron.

The accuracy of the method depends upon the uniformity of conditions of temperature, concentration, etc., of making the run with the sample and of standardizing the stannous chloride. The solution should be free from other oxidizing agents, or from salts that give colored solutions.

The amount of iron in terms of ferric oxide that can be estimated by this procedure ranges from 0.002 gram to 0.05 gram.

**Reagents. — Stannous Chloride Solution.** — The reagent is prepared by dissolving 2 grams of stannous chloride crystals in hot concentrated hydrochloric acid and making up to 1 liter. The solution should be kept in a dark bottle to which the titrating burette is attached in such a way that the liquid may be siphoned out into this, as shown in the illustration, Fig. 83. The air entering the bottle passes through phosphorous or pyrogallic acid to remove the oxygen. In this way, protected from the air, the reagent will keep nearly constant for several weeks. It is advisable, however, to restandardize the solution about every ten to fifteen days. One cc. will be equivalent to about 0.001 gram of Fe.

**Standard Iron Solution.** — 8.6322 grams of ferric ammonia alum is dissolved in dilute hydrochloric acid and made up to one liter. The iron is determined in 100 cc. portions by the dichromate method. One cc. will contain about 0.001 gram of Fe.

**Procedure.** — To the sample in a casserole is added 25 cc. of concentrated hydrochloric acid and an equal volume of water. The resulting solution is heated to boiling and quickly titrated with the stannous chloride reagent, until the yellow color fades out and the solution becomes colorless.

Note. The titration should be done quickly, as the iron will reoxidize on standing and the solution again become yellow. The true end-point is the first change to a colorless solution.

## COLORIMETRIC METHOD FOR DETERMINING SMALL AMOUNTS OF IRON

### Sulphocyanate (Thiocyanate) Method [1]

**Introduction.** — By this method 1 part of iron may be detected in 50 million parts of water. The presence of free mineral acid increases the sensitiveness of the method, so that it is especially applicable to the determination of small amounts of iron in mineral acids. It is available in presence of many of the ordinary metals and in presence of organic matter. Silver, copper, cobalt, mercuric chloride, however, interfere. Nitric acid gives a color with sulphocyanate.

This method, like the stannous chloride method, determines only the ferric iron. It is based on the fact that ferric iron and an alkali sulphocyanate, ammonium or potassium sulphocyanate, in an acid solution give a red color, the intensity of which is proportional to the quantity of iron present. The color is due to the formation of the compound, $Fe(CNS)_3.9KCNS.4H_2O$.

**Reagents Required. — Standard Iron Solution.** — A ferric solution, the iron content of which has been determined, is diluted and divided so as to obtain 0.0004 gram of Fe. This is made up to 2 liters with water containing 200 cc. of iron-free, C.P. $H_2SO_4$. One hundred cc. of this solution, together with 10 cc. of normal ammonium sulphocyanate solution, is used as a standard. One hundred cc. contains 0.00002 gram of Fe.

Normal sulphocyanate contains 76.1 grams of $NH_4CNS$ per liter.

**Procedure.** — The weighed sample, 1 to 10 grams, or more if necessary, is dissolved in dilute $H_2SO_4$ and oxidized by adding dilute permanganate, $KMnO_4$, solution drop by drop until a faint pink color is obtained. The sample is diluted to exactly 100 cc. and is poured into a burette graduated to 0.1 cc. Two colorless glass cylinders of the 100-cc., Nessler type are used for comparison of standard and sample. Into one cylinder is poured 100 cc. of the standard solution, made as directed above. Into the second cylinder containing 10 cc. of sulphuric acid with 10 cc. of ammonium sulphocyanate, $NH_4CNS$, diluted to 60 or 70 cc., the sample is run from the burette until the depth of the color thus produced on dilution to 100 cc. exactly matches the standard. From the number of cc. used the weight of the sample is calculated. One hundred cc. of the standard contains 0.00002 gram Fe.

Dividing the weight of iron in the standard by the weight of sample used and multiplying by 100 gives the per cent of iron in the sample.

Notes. If other metals are present, that form two series of salts, they must be in the higher state of oxidation, or the color is destroyed. (Sutton.) Oxalic acid, if present, destroys the color. Oxidation with $KMnO_4$ or $KClO_3$ with subsequent removal of $Cl_2$ prevents this interference. (Lunge, C. N., 73, 250.)

Chlorides of the alkaline earths retard or prevent the sulphocyanate reaction. (Weber, C. N., 47, 165.)

[1] Thomson, J. C. S., 493, 1885, and C. N., 51, 259. Kruss and Moraht, C. N., 64, 255. Davies, C. N., 8, 163.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### TECHNICAL ANALYSIS OF IRON AND STEEL

The elements carbon, manganese, phosphorus, sulphur, and silicon are invariable constituents of iron and steel, and are always included in an analysis. Copper and arsenic are sometimes found; aluminum, chromium, nickel, molybdenum, tin, titanium, tungsten, vanadium, and zinc occur in special alloy steels. Minute traces of oxygen, hydrogen, and of many other elementary constituents frequently are present, but are of so little importance that they are seldom considered in an analysis.

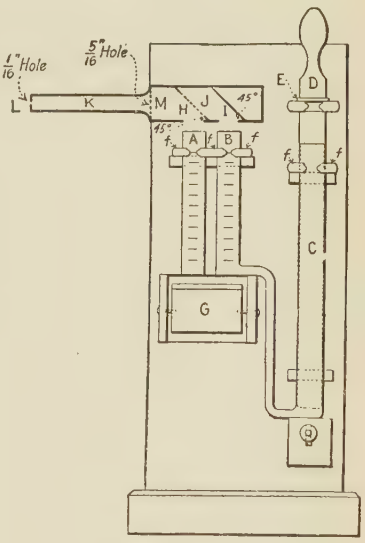



FIG. 84.

Our attention is drawn in this chapter to the more important constituents, whose estimation is required in the daily routine analysis of a steel works laboratory. The elements considered are carbon — carbide or combined carbon and graphitic carbon, manganese, phosphorus, sulphur, and silicon. Determination of the elements of special alloy steels containing aluminum, chromium, nickel, titanium, tungsten, vanadium, etc., are given in the chapters on the elements in question; for example the determination of vanadium in steel will be found in the chapter on Vanadium, chromium and copper in the chapters on Chromium and Copper, etc.

FIG. 85. Dividing Pipette.

As is generally the case, a large number of determinations are required in the steel works laboratories and it is not an uncommon thing for one man to turn out 50 to 100 determinations a day. To accomplish this, simple and rapid procedures are required. When the metal is unusually high in an undesirable constituent it is indicated by the test, and a confirmation of the result is obtained by an additional test, exercising extreme care, and using a procedure giving results of the highest accuracy. Fortunately the analysis of steel has received considerable attention and rapid methods have been worked out which are extremely accurate.

The procedures briefly outlined have proven of value to analysts of iron and steel. While in charge of the laboratory at Baldwin Locomotive Works, the author found that a skilled analyst was able to turn out 125 determinations of combined carbon, or 100 of manganese, or of sulphur, or 50 determinations of phosphorus, or 25 determinations of silicon per day by the procedures given. This necessitates the use of a large number of beakers and flasks, ample desk room, individual balances, hot plates, and hoods to accommodate a dozen to two dozen beakers or flasks at a time, and a carefully planned system.

The dividing pipette, shown in Fig. 85, is useful for adding a definite amount of reagent to the sample.

### Preparation of the Sample

The metal is sampled by drilling with a clean twist drill, using no water or oil.

Hard grades of pig iron, chilled iron, ferromanganese, quenched steel, etc., are broken down to a coarse powder in a chilled steel mortar.

## DETERMINATION OF CARBON

### Combined or Carbide Carbon — Colorimetric Method

**Rapid Method.** — 0.2 to 0.5 gram of drillings is placed in a test-tube, $6 \times \frac{3}{4}$ ins., and 5 to 20 cc. of nitric acid (sp.gr. 1.2) added from a burette, the test-tube being placed in cold water to prevent too violent action. The amount of acid added is governed by the carbon-content of the steel (see chapter on Carbon). After the violent action has ceased, the tube is placed in a specially-designed water bath, the water heated to boiling and boiled for twenty minutes or more until the solution in the tube has become perfectly clear. The sample is now removed, washed into a color carbon tube and compared with a standard steel of the same class of material as that examined under the same conditions. Full details of the procedure may be found in the chapter on Carbon.

Iron and steel containing graphite must be filtered before making comparisons. The solution, diluted with one-half its volume of water, is filtered through a small filter paper into a test-tube. The residue is washed with a fine jet of distilled water until free of color. The filtrate is compared with a standard sample of similar composition treated in the same way.

Steel containing chromium, copper, nickel, and elements yielding a colored solution should not be examined by the colorimetric methods.

**Method of the Bureau of Standards.** — Total and graphitic carbon are determined and the difference taken as combined carbon.

### Total Carbon

The determination is required for an accurate estimation of carbon where the color test indicates the carbon content outside the limits of requirement, or in cases where interfering substances are present. In material where the carbon content is of extreme importance, the color method is not used. Details of the procedure for determining carbon by direct combustion are given in the chapter on Carbon. The following procedure is recommended by the Bureau of Standards:

(*a*) **In Irons.** — Two grams of iron are mixed with about twice the weight of purified ferric oxide. The mixture is placed in a platinum boat, which is lined with a suitable bed material, such as alundum, and is burned in a current of oxygen, as described below.

(*b*) **In Steels.** — The method is the same as for irons with omission of the ferric oxide mixture.

**Details of Direct Combustion Method. — Furnaces and Temperature of Burning.** — Porcelain tubes wound with "nichrome" wire, provided with suitable heat insulation and electrically heated, are used, and readily give temperatures to 1100° C. The temperature

control is by means of an ammeter and rheostat in series with the furnace, with occasional check by a thermocouple.

**Boats and Lining.** — Platinum boats provided with a long platinum wire for manipulation in the tube are mostly used; alundum ones occasionally. The bed or lining on which the steel rests is 90-mesh "RR alundum, alkali-free, specially prepared for carbon determination." A layer of this alundum is also placed in the bottom of the combustion tube to prevent the boat sticking to the glaze. A platinum cover for the boat is sometimes used, and is essential when the combustion is forced.

The nature and quality of the bed material are matters of great importance. Alumina as prepared from the sulphate or from alum may not be free from sulphate or alkali, both of which have given serious trouble at the Bureau. The alkali, if present, may not manifest itself by an alkaline reaction until after one or two combustions have been made, using the same bed material. Even the ordinary white "alundum" on the market carries a few hundredths of 1% of alkali. Iron oxide has been tried, and when pure should, apparently, give good service. As yet, however, it has been difficult to obtain or prepare acceptable material for use with steels. Quartz sand gives rise to a fusible slag, which melting before combustion is complete, incloses bubbles of carbon dioxide gas. This defect would probably inhere in any other material of an acid character. The presence in the silica bed after combustion of crystals which appear to be carborundum, have occasionally been noted.

**Purity of Oxygen. — Blanks.** — The Bureau makes its oxygen electrolytically, and its content of this element is usually 99 to 99.5%, and sometimes higher. Even with this gas a slight blank is usually obtained. When running a blank in addition to the usual proportions, the rate at which the oxygen is introduced should be the same as when burning a sample, and the time should be three to five times as long.

**Method of Admitting Oxygen and Rate of Combustion.** — The furnace being at the proper temperature, the boat containing the sample is introduced. Oxygen is admitted either at once or after the boat has reached the temperature of the furnace, as the operator prefers, or as the nature of the steel may demand. The rate of flow of the oxygen varies with the absorption apparatus used and with the preference of the operator, and may be considerably more rapid when absorbing carbon dioxide in soda lime than in an alkaline solution. A rapid flow of oxygen also facilitates the burning of resistant samples. A continuous forward movement of the gas current is maintained at all times. The time for a determination varies, of necessity, with the nature of the sample and the rate of flow of the oxygen, ranging from ten to thirty minutes. The endeavor is to obtain a well-fused oxide. With all samples close packing in a small space is conducive to rapid combustion and to fusion of the resulting oxide.

Authorities differ as to the advisability of allowing the oxide of iron to fuse thoroughly. Even when fusion does take place additional carbon dioxide is obtained very frequently by grinding the oxide and reburning. Often more than one regrinding and reburning is necessary in order to reduce the amount of carbon dioxide obtained to that of the constant blank.

Oxides of sulphur have been found very difficult to eliminate from the gases leaving the tube. Lead peroxide heated to 300° C. and zinc at room temperature appear to retain them best.

Attention is called to the inadmissibility of using dry agents of different absorptive power in the same train, in positions where a difference could possibly affect results.

**Weighing of Tubes.** — There is much greater difficulty in securing constant conditions when weighing absorption tubes than is usually considered to be the case. Electrical effects, caused by wiping as a preliminary to weighing, may occasionally cause errors in weight running into the milligrams. The use of counterpoises of equal volume and similar material and shape is recommended.

If tubes are weighed full of oxygen, care is necessary to secure a uniform atmosphere in them. Even though the attempt is made to keep the apparatus always full of oxygen, some air is admitted when the boat is pushed into the combustion tube, and a much longer time is required to displace this than is usually allowed, unless the flow of oxygen during aspiration is rapid. The same is true if the tubes are weighed full of air by displacing the oxygen left in them after the steel is burned. Another source of error may arise from the air admitted when putting the boat into the tube, if this air contains much carbon dioxide, as is the case when a gas furnace is used. The boat is usually pushed at once into the hot furnace, and as combustion begins almost immediately, there is no opportunity for displacing this air before the steel begins to burn.

### Graphite in Iron

Two grams of iron are dissolved in nitric acid (sp.gr. 1.20), using 35 cc. and heating very gently. The residue is collected on an asbestos felt, washed with hot water, then with a hot solution of potassium hydroxide (sp.gr. 1.10), followed by dilute hydrochloric acid and finally by hot water. After drying at 100° C., the graphite is burned in the same manner as the total carbon, but without admixture of ferric oxide.

## MANGANESE IN IRON AND STEEL

### Ammonium Persulphate Method

Small amounts of manganese may be determined colorimetrically by the persulphate method, provided the sample does not contain over 1.5% of manganese.

**Reaction.** $2Mn(NO_3)_2 + 5(NH_4)_2S_2O_8 + 8H_2O = 5(NH_4)_2SO_4 + 5H_2SO_4 + 4HNO_3 + 2HMnO_4$.

0.1 to 0.2 gram of steel, according to the amount of manganese in the sample, is placed in a 10 in. test-tube and 10 cc. of nitric acid (sp.gr. 1.2) are added. The sample is heated in a water bath until the nitrous fumes are driven off and the steel is completely in solution. 15 cc. of $AgNO_3$ sol. (1.5 g. per l.) are added to the cooled sample, followed immediately with about 1 gram of ammonium persulphate crystals. The solution is warmed (80 to 90° C.) until the color commences to develop, and then for half a minute longer, and then placed in a beaker of cold water until the solution is cold. Comparison is now made with a standard steel treated in the same way. The comparison being made exactly as indicated for determining carbon by the color method. See chapter on Carbon.

**Example.** — If the standard, containing 0.6% Mn is diluted to 15 cc. each cc. = 0.04% Mn. If the sample required a dilution of 20 cc. to match the standard, then $0.04 \times 20 = 0.8\%$ Mn.

Note. If preferred, the sample may be titrated with standard sodium arsenate, one cc. of which is equivalent to 0.1 per cent on basis of 0.1 gram sample.

### Lead Oxide Method (Deshey).

Oxidation of the manganese in the steel is effected in a nitric acid solution by addition of red lead (or by lead peroxide); the lead peroxide, formed, oxidizes the manganese nitrate to permanganic acid. The solution is now titrated with standard sodium arsenite, the following reaction taking place:

$$2HMnO_4 + 5Na_3AsO_3 + 4HNO_3 = 5Na_3AsO_4 + 3H_2O + 2Mn(NO_3)_2.$$

0.5 gram of steel is placed in a 150 cc. beaker and dissolved with about 30 cc. of nitric acid (sp.gr. 1.12). After violent action has subsided, the beaker is placed on a hot plate and when the iron has dissolved, 20 cc. of water added. The manganese is now oxidized by adding red lead in small portions at a time, until the solution appears brown with a pinkish purple foam on the surface. The solution is diluted with hot water until the volume is about 100 cc. and then boiled for a few minutes. It is now placed in a dark closet to cool.

(A fresh batch of samples may be started in the meantime.) The solution is carefully decanted off from the peroxide, and with the washings of the peroxide residue, titrated with standard sodium arsenite to the yellowish green end-point. The sodium arsenite is made by dissolving 4.96 grams of pure arsenous acid together with 25 grams of sodium carbonate in 200 cc. of hot water and the solution diluted to 2500 cc. The arsenite is standardized against a steel sample of known manganese content, or against standard permanganate solution.

### Bismuthate Method for Determining Manganese, Recommended by the U.S. Bureau of Standards

This is the most accurate method for determining manganese in iron and steel. The procedure is as follows:

**Procedure.** — One gram of drillings is dissolved in 50 cc. of nitric acid (sp.gr. 1.135) in a 200 cc. Erlenmeyer flask. Irons should be filtered. The solution is cooled, about 0.5 gram of sodium bismuthate is added, and it is then heated until the pink color has disappeared. Any manganese dioxide separating is dissolved in a slight excess of a solution of ferrous sulphate or sodium sulphite. The solution is boiled till free from nitrous fumes. After cooling to 15° C., a slight excess of bismuthate is added and the flask is shaken vigorously for a few minutes. Then 50 cc. of 3% nitric acid is added and the solution is filtered through asbestos. A measured excess of ferrous sulphate is run in and the excess titrated against permanganate solution which has been compared with the iron solution on the same day. A great many steels now carry small amounts of chromium as impurity. In such cases titration against arsenite solution is recommended, or removal of the chromium by zinc oxide and subsequent determination of the manganese by the bismuthate method.

Permanganate solutions are standardized against sodium oxalate.

## DETERMINATION OF PHOSPHORUS

The procedures outlined by the Bureau of Standards are generally used in steel works laboratories.

(*a*) **Preparation of Solution and Precipitation of Phosphorus.** — Two grams of sample are dissolved in nitric acid (sp.gr. 1.135) and the solution is boiled until brown fumes no longer come off. Ten cc. of permanganate solution (15 grams to 1 liter) are added, and the boiling is continued. Sodium sulphite solution is added to dissolve the oxide of manganese, and the solution is again boiled and then filtered. With irons the insoluble residue should be tested for phosphorus. After cooling the filtrate, 40 cc. of ammonia (sp.gr. 0.96) are added, the solution is agitated, and when the temperature is at 40° C., 40 cc. of molybdate solution are added and the solution is shaken vigorously for five minutes. After settling out, the yellow precipitate is treated according to one of the following methods, *b* or *c:*

(*b*) **Alkalimetric Method.** — The precipitate is washed with 1% nitric acid solution followed by 1% potassium nitrate solution until the washings are no longer acid. The precipitate is dissolved in a measured excess of standardized sodium hydroxide solution and titrated back with standardized nitric acid using phenolphthalein. The solutions are standardized against a steel with a known amount of phosphorus.

(*c*) **Molybdate Reduction Method.** — The precipitate is washed ten to fifteen times with acid ammonium sulphate (see chapter on phosphorus) or until the washings no longer react for iron or molybdenum. It is dissolved in 25 cc. of ammonia (5 cc. of ammonia of 0.90 sp.gr. to 20 cc. of water). The filter is washed well with water and 10 cc. of strong sulphuric acid added to the filtrate, which is run through the reductor at once and titrated against a N/30 permanganate solution which has been standardized against sodium oxalate, as prescribed by McBride.[1]

[1] Bull. Bur. Stds., 8, 641. J. Am. Chem. Soc., 34, 393, 1912.

## DETERMINATION OF SULPHUR

**Rapid-evolution Method. — Volumetric.** — Five grams of iron or steel are placed in a 500 cc. Erlenmeyer flask, provided with a two-holed rubber stopper, through which passes a long-stem thistle tube reaching to the bottom of the flask, and a delivery-bulb condenser, connected by means of a rubber tube to an absorption bulb. (See sketch of apparatus in the chapter on Sulphur, volumetric methods.)

About 25 to 35 cc. of an ammoniacal solution of cadmium chloride are placed in the absorption bulb, the apparatus connected and about 100 cc. of dilute hydrochloric acid (sp.gr. 1.1) poured through the thistle tube into the flask containing the drillings. The mixture is heated gently until the sample goes into solution and then boiled until steam escapes from the apparatus. The reagent in the absorption bulb should remain alkaline, otherwise a loss of sulphur is apt to occur.

The absorption bulb is now disconnected and the contents emptied into a 400 cc. beaker and the bulb washed out with dilute hydrochloric acid after first rinsing out once or twice with water. The solution is now diluted to about 300 cc., and if not already acid, is made so by addition of more hydrochloric acid.

Two to 3 cc. of starch indicator are added and the mixture titrated with standard iodine, stirring constantly during the titration. A permanent blue color is the end-point sought. If much cadmium sulphide is present additional hydrochloric acid may be required.

The number of cc. of iodine solution required multiplied by the factor of iodine to sulphur gives the amount of sulphur present in the sample taken.

Notes. For a more complete description of the procedure see chapter on Sulphur.

With certain pig irons low results are apt to be obtained by the evolution method. For such the gravimetric method given is recommended.

Gray iron will evolve all its sulphur as $H_2S$, white iron, gray water-chilled iron, gives up only part of its sulphur by the evolution method. The method gives low results for high carbon steel.

In place of absorbing the $H_2S$ in cadmium chloride, the Bureau of Standards recommends absorption in an ammoniacal solution of hydrogen peroxide (5 cc. $H_2O_2$ 3% + 25 cc. of $NH_4OH$, sp.gr., 0.90). The sulphuric acid formed is precipitated from a slightly hydrochloric acid solution, by barium chloride and weighed as $BaSO_4$. Bureau of Standards Steel No. 8 (a) is recommended for standardizing the iodine or iodate. (See following method.)

*Optional Method.* In place of the bulb for the $CdCl_2$ solution an ordinary beaker may be used with this solution (10 cc. $CdCl_2$ sol. per 150 cc. $H_2O$). The sulphide is now titrated, in presence of starch indicator, after acidifying with HCl by addition of potassium iodate (1.116 g. $KIO_3$ + 12 g. KI in 1000 cc. $H_2O$). The reagent is standardized against a steel of known sulphur content. Each cc. is equivalent to .01% S on 5.0 gram sample.

### Method by the U.S. Bureau of Standards. Gravimetric Sulphur by Oxidation

Five grams of iron or steel are dissolved in a 400-cc. Erlenmeyer flask, using 50 cc. of strong nitric acid. A little sodium carbonate is added, the solution is evaporated to dryness, and the residue baked for an hour on the hot plate. To the flask 30 cc. of strong hydrochloric acid are added, and the evaporation and baking are repeated. After solution of the iron in another 30 cc. of strong hydrochloric acid and evaporation to a sirupy consistency, 2 to 4 cc. of the same acid are added, followed by 30 to 40 cc. of hot water. The solution is then filtered and the residue washed with hot water. The sulphur is precipitated in the cold filtrate (about 100 cc.) with 10 cc. of a 10% solution of barium chloride. After forty-eight hours the precipitate is collected on a paper filter, washed first with hot acid (containing 10 cc. of concentrated hydrochloric acid and 1 gram of barium chloride to the liter) until free from iron and then with hot water till free from chloride; or, first with cold water, then with 25 cc. of water containing 2 cc. of concentrated hydrochloric acid to the liter. The washings are kept separate from the main filtrate and are evaporated to recover dissolved barium sulphate.

With iron the paper containing the insoluble residue above mentioned is put into a platinum crucible, covered with sodium carbonate free from sulphur, and charred without allowing the carbonate to melt. The crucible should be covered during this operation. Sodium nitrate is then mixed in and the mass fused with the cover off. An alcohol flame is used throughout. The melt is dissolved in water and evaporated with hydrochloric acid in excess to dryness in porcelain. The evaporation with water and hydrochloric acid is repeated to insure removal of nitrates. The residue is extracted with a few drops of hydrochloric acid and water, the insoluble matter is filtered off, and barium chloride is added to the filtrate. The barium sulphate obtained is added to the main portion.

Careful blanks are run with all reagents.

## DETERMINATION OF SILICON

One gram of pig iron, cast iron, and high silicon iron, or 5 grams of steel, wrought iron, and low silicon iron are taken for analysis. (By taking multiples of the factor weight 0.4693, $SiO_2$ to Si, the final calculation is simplified.) The sample is placed in a 250 cc. beaker and 20 to 50 cc. of dilute nitric acid added. If the action is violent, cooling the beaker in water is advisable. When the reaction subsides, 20 cc. of dilute sulphuric acid, 1 : 1, are added, the mixture placed on the hot plate and evaporated to dense white fumes. The residue is taken up with 150 cc. of water containing 2 to 5 cc. of sulphuric acid and heated until the iron completely dissolves.

The solution is filtered and the silica residue washed first with hot dilute hydrochloric acid, sp.gr. 1.1, and then with hot water added in small portions to remove the iron sulphate. The residue is now ignited and weighed as silica.

If there is any doubt as to the purity of the silica, moisten the residue (in a platinum crucible) with strong sulphuric acid and add a few cc. of hydrofluoric acid (crucible cover full), evaporate to dryness, ignite and weigh. The loss of weight is due to silica.

Note. If the ash is colored by iron oxide, silica is determined by difference after expelling the silica by adding 4 to 5 cc. of hydrofluoric acid and a few drops of sulphuric, taking to dryness and igniting the residue.

The following acid mixtures are recommended by the U. P. Ry. For steel, wrought iron and low silicon iron, 8 parts by volume of $HNO_3$, sp.gr. 1.42; 4 parts of conc. $H_2SO_4$, sp.gr. 1.84; 6 parts HCl, sp.gr. 1.2 and 15 parts by volume of water. For dissolving pig iron, cast iron and high silicon iron, a mixture of 8 parts by volume of strong nitric acid and 5 parts of strong sulphuric acid, diluted with 17 volumes of water is used.

**Rapid Method for Determining Silicon in Foundry Work.** Liquid iron, dropped into cold water from a ladle 3 ft. above the water, will form shot shaped according to forms resulting from its chemical constitution, silicon being an important factor. Round shot, concave upper surface, 1 to 3 in. in diameter, indicate over 2% silicon. Flat, or irregular shot indicate low silicon. Shot with elongated tails indicate very low silicon.

### Method of the U.S. Bureau of Standards for Silicon

The insoluble residue obtained in preparing the iron or steel for the gravimetric sulphur determination is filtered off, ignited in platinum, and weighed. Evaporation with a little hydrofluoric acid and 1 drop of sulphuric acid and subsequent ignition gives by the loss of weight silica corresponding to the silicon of the sample.

**Other Methods for Determination of the Less Common Elements in Steel.** — Other elements more commonly sought in alloy steel are copper, nickel, chromium, vanadium, tungsten, titanium and molybdenum. Methods for estimation of these elements are given in the chapters dealing with these substances.

## LEAD

**Pb, at.wt. 207.2; sp.gr. 11.34; m.p. 327°; b.p. 1525° C; oxides, PbO, $PbO_2$, $Pb_3O_4$.**

The determination of lead is required in valuation of its ores. It is determined in lead mattes; certain slags; drosses from hard lead; cupel bottoms; skimmings; lead insecticides (arsenate of lead); paint pigments such as white lead, red lead, yellow and red chromates, etc. It is determined in alloys such as solder, type metal, bell metal, etc. The estimation is necessary in the complete analysis of a large number of ores, especially in minerals of antimony and arsenic. Traces of lead are determined as an impurity in certain food products.

### OCCURRENCE

Lead is found native in comparatively small amounts and combined in a large number of minerals principally as a sulphide in galenite or galena.

**Minerals.** — *Native lead*, Pb, a soft, malleable, opaque mineral with metallic lustre; color and streak, lead-gray; usually in small plates or scales, or globular masses, embedded in other minerals; hardness 1.5. Occasionally alloyed with antimony or silver.

*Galenite, Galena*, PbS, a soft, heavy, lead-gray mineral, with metallic lustre; opaque; brittle with cubic cleavage, sometimes in crystals, rarely fibrous or fine-grained; hardness 2.5. The granular variety (steel galena) usually carries silver, sulphide of cadmium, bismuth, antimony.

*Cerussite*, $PbCO_3$, an adamantine, silky-lustred mineral, white or colorless orthorhombic crystals, masses of interlaced fibres, compact or earthy; colorless, white, gray or colored by impurities; transparent to translucent; brittle; hardness 3–3.5. Silver often present.

*Anglesite*, $PbSO_4$, a mineral with adamantine to vitreous lustre; transparent to opaque; colorless, gray, occasionally blue, green or yellow; white streak; brittle; hardness 3.

*Pyromorphite*, $Pb_4(PbCl)(PO_4)_3$ a mineral with hexagonal prisms, branching groups in parallel position, also moss-like interlaced fibres, occasionally globular and reniform masses; color white, green, gray, brown, yellow orange, with white to yellow streak; resinous lustre; translucent to opaque; brittle; hardness 3.5–4.

*Other Minerals — Minium*, $Pb_3O_4$; *Phosgenite*, $PbCO_3.PbCl_2$, *Vanadinite*, $Pb_4(PbCl)(VO_4)_3$; *Crocoite*, $PbCrO_4$; *Wulfenite*, $PbMoO_4$; *Clausthalite*, PbSe.

### SUGGESTIONS TO STUDENTS

For the gravimetric procedure determine lead by the chromate method, page 342. If a volumetric method is desired follow either the permanganate or the chromate-iodide method, pages 345, 348.

### DETECTION

For qualitative tests a small amount of the substance finely divided is dissolved in dilute nitric acid and tests made with the reagents indicated. It is not necessary to get a complete solution of the substance, but the residue should be saved in case the tests of the acid extract are negative.

Insoluble residues are fused with a mixture of sodium and potassium carbonates, the cooled mass extracted with hot water and the carbonate remaining dissolved in dilute nitric acid and tested for lead. This is unnecessary if the acid extract has proven the presence of lead.

Hydrochloric acid precipitates from cold solution, sufficiently concentrated, a white precipitate of lead chloride, $PbCl_2$, if lead is present. The precipitate dissolves on heating the solution, but on cooling needle-like crystals are reprecipitated.

**Potassium chromate,** added to the acid solution which has been neutralized with sodium or ammonium acetate, precipitates yellow lead chromate, practically insoluble in acetic, but soluble in strong mineral acids, soluble in excess of caustic soda.

**Sulphuric acid,** produces a white precipitate of lead sulphate, $PbSO_4$, soluble in hot concentrated hydrochloric or sulphuric acids, soluble in sodium or ammonium acetates, sodium thiosulphate, and certain other salt solutions. Solubility is decreased by presence of sulphuric acid and alcohol.

**Hydrogen sulphide** produces a black precipitate of lead sulphide, PbS, soluble in dilute nitric acid. If the gas is added to a nitric acid solution free sulphur will first precipitate. Lead sulphide is converted to sulphate by strong nitric acid.[1]

**Sodium carbonate,** precipitates white lead carbonate, $PbCO_3$, insoluble in excess of the reagent, soluble in acetic acid. A solution of sodium carbonate poured over lead sulphate will transpose it to carbonate, sodium sulphate passing through the filter. The carbonate should be in large excess.

**Zinc** added to a solution of lead will precipitate spongy metallic lead.

NOTE. Galena and sulphides may be prepared for the tests by treating with nitric acid, evaporating to dryness after adding a few drops of dilute sulphuric acid and extracting the residue with sodium or ammonium acetate solution. The extract is tested for lead, by addition of potassium dichromate solution.

[1] Lead precipitates best from solutions containing 1 cc. of concentrated free hydrochloric acid (sp.gr. 1.19) for each 100 cc. of solution. The sulphide is appreciably soluble if the acidity is increased to 3 cc. of HCl per 100 of solution.

### Dry tests

The powdered substance mixed with 5–6 times its bulk of sodium-potassium carbonate and heated on charcoal in the reducing flame yields a bead of metallic lead, which marks paper, the incrustation of the lead oxide on the charcoal is yellow.

An asbestos fibre dipped in the substance moistened with hydrochloric acid and held in the oxidizing flame of the Bunsen burner tinges the flame a faint blue.

## METHODS FOR DETERMINING LEAD

### Preparation and Solution of the Sample

In dissolving lead, its alloys, or ores the following facts will be recalled. Hot, dilute nitric acid is the best solvent of the metal. Lead nitrate is insoluble in concentrated nitric acid, but dissolves readily upon dilution with water. The metal is insoluble in dilute sulphuric acid, but dissolves in the hot, concentrated acid. Although not soluble in dilute hydrochloric, it dissolves in the hot, concentrated acid, especially in presence of the halogens chlorine, bromine and iodine. The metal is soluble in glacial acetic acid. The salts are soluble in hot, dilute nitric acid. In dissolving sulphide ores it should be kept in mind that strong nitric acid will form some lead sulphate which will be precipitated upon dilution of the solution. Oxidation is less apt to occur with the dilute acid. Silicates and slags require fusion with sodium carbonate and potassium carbonate. The cooled mass may then be extracted with hot water to remove silica and the residue containing the carbonates of the heavy metals dissolved in dilute nitric acid. Lead salts are soluble in ammonium acetate.

#### Ores

**Oxides, Carbonates.** — The substances are generally soluble in dilute nitric acid; the substance should be finely divided.

**Sulphides.** — It is often advisable to start with hydrochloric acid to expel the hydrogen sulphide and follow this with nitric acid, or the ore may be treated with a mixture of sulphuric and nitric acids in the proportion of 1 : 3, and after the violent action has ceased (beaker covered) if silica is present a little hydrofluoric acid, in an amount that would fill a platinum crucible cover, is added. The mixture is evaporated to sulphuric acid fumes (hood) then diluted with distilled water (about 100 cc.) and digested on a steam bath or hot plate until the soluble salts are in solution. The lead sulphate is filtered off, and washed with dilute sulphuric acid (1 : 15). The residue is dissolved in sodium or ammonium acetate and determined by one of the procedures under the methods.

**Silicates and Slags.** — These may be decomposed by fusion with sodium and potassium carbonates. The mass is extracted with water and the residue containing the lead is dissolved in dilute nitric acid.

If preferred the silicates may be decomposed by treating with hydrofluoric acid and sulphuric acid. The solution is evaporated to white fumes and the lead sulphate taken up with water, filtered off, washed with dilute sulphuric acid and finally once with water (preferably containing about 25–50 per cent of alcohol). The sulphate is then extracted with acetate, lead going into solution.

**Alloys.** — These are best decomposed by treatment with dilute nitric acid. The lead may be subsequently converted to sulphate by addition of sulphuric acid.

### Methods of Isolating Lead

**Separation of Lead as Sulphate.** — Lead is most frequently separated from other metals by precipitation as sulphate, $PbSO_4$, according to the details given under "Preparation and Solution of the Sample." In the presence of much bismuth or iron it is necessary to wash the precipitate with a 10% sulphuric acid solution to keep the bismuth in solution and to prevent the formation of the difficultly soluble basic ferric sulphate. In absence of appreciable amounts of these elements the lead sulphate is more completely separated by adding to the dilute sulphuric acid solution an equal volume of alcohol, filtering and washing the residue with 50% alcohol.

**Separation of Lead from Barium.** — In the analysis of minerals containing barium, the insoluble sulphate, $BaSO_4$, will be precipitated with lead. Since barium sulphate is slightly soluble in ammonium acetate it will contaminate the lead in the subsequent extraction by this reagent. The presence, however, of a little sulphuric acid renders this solubility practically negligible. The sulphuric acid should not exceed 1–2% in the ammonium acetate reagent, as lead sulphate will precipitate if sufficient sulphuric acid is added to the acetate extract. (Lead sulphate is precipitated almost completely if the acetate solution contains 10% of sulphuric acid.)

Lead may be separated from barium sulphate by digesting the mixed sulphates with ammonium carbonate solution, whereby the lead sulphate is transposed to lead carbonate and ammonium sulphate, while barium sulphate is not changed. The soluble ammonium sulphate may be washed out with ammonium solution followed by water. Since lead carbonate is slightly soluble in the ammonium salt, the filtrate is treated with hydrogen sulphide and the dissolved lead recovered as PbS. The residue containing lead carbonate and barium sulphate is treated with dilute nitric or acetic acid. Lead passes into solution, while barium sulphate remains insoluble.

**Extraction of Lead from the Impure Sulphate by Ammonium Acetate.** — The filter containing the impure sulphate, obtained by one of the procedures for solution of the sample, is placed in a casserole and extracted with about 50 cc. of hot, slightly ammoniacal ammonium acetate, the stronger the acetate the better. The clear liquid is decanted through a filter and the extraction repeated until the residue is free from lead (i.e., no test is obtained for lead with $K_2Cr_2O_7$). A very effective method of extraction is by adding solid ammonium acetate directly to the sample on a filter and pouring over it a hot solution of ammonium acetate. The filtrate containing the pure lead acetate solution may now be examined by one of the following procedures. (For isolation of minute quantities see page 356.)

Lead sulphate containing arsenic should be dissolved in ammonium acetate, the extract made alkaline and lead precipitated as PbS. Arsenic remains in solution.

## GRAVIMETRIC METHODS

### DETERMINATION OF LEAD AS THE SULPHATE, $PbSO_4$

**Procedure.** — The sample having been dissolved according to a method outlined, the lead precipitated as $PbSO_4$ by addition of an excess of sulphuric acid, and taking to $SO_3$ fumes, the lead sulphate is filtered off, after cooling and diluting the sample. The $PbSO_4$ is washed with water containing 10% of $H_2SO_4$ until free from soluble impurities. If insoluble sulphates or silica are present the lead must be purified. If such impurities are known to be absent (alloys), the sulphate may be filtered directly onto an asbestos mat in a tared Gooch crucible, dried, then ignited to dull red heat, cooled and finally weighed as $PbSO_4$. In the analysis of ores, however, it is generally advisable to purify the sulphate.

**Purification of Lead Sulphate.** — Details of the procedure have been given under Separations — Extraction of Lead from the Impure Sulphate. The lead sulphate having been brought into solution by extraction with strong ammonium acetate solution, the excess acetic acid is volatilized by evaporation, the residue cooled and diluted with water. An excess of sulphuric acid is added and the precipitated sulphate is filtered off, washed with dilute sulphuric acid and alcohol, dried at about 110° C., or if preferred by ignition at dull red heat, and weighed.

$$PbSO_4 \times 0.6831 = Pb.$$

Notes. Lead sulphate may be precipitated from ammonium acetate solution by adding sulphuric acid until the solution contains approximately 10% of $H_2SO_4$.

An acetate extraction may not be necessary, as is generally the case in the analysis of alloys. In analysis of ores, however, $PbSO_4$ may be contaminated by sulphates of the alkaline earths and by silica. The difficultly soluble oxides of iron and alumina may also be present.

If arsenic is in the sulphate it will pass into the filtrate with the lead.

### DETERMINATION OF LEAD AS THE CHROMATE, $PbCrO_4$

This excellent method is applicable to a large class of materials and is of special value in precipitation of lead from an acetic acid solution, the method depending upon the insolubility of lead chromate in weak acetic acid.

**Procedure.** — The solution of the sample, precipitation of the lead as the sulphate and extraction of lead with ammonium acetate have been given in detail.

The filtrate, containing all the lead in solution as the acetate, is acidified slightly with acetic acid and heated to boiling. Lead is precipitated by addition of potassium dichromate solution in excess (10 cc. of 5% $K_2Cr_2O_7$ solution are generally sufficient). The solution is boiled until the yellow precipitate turns to a shade of orange or red.[1] The precipitate is allowed to settle until the supernatant solution is clear. (This should appear yellow with the excess of dichromate reagent.) The $PbCrO_4$ is filtered onto an asbestos mat in a tared Gooch crucible, washed with water, dried in an oven at about 110° C. and the cooled compound weighed as $PbCrO_4$.

$$PbCrO_4 \times 0.641 = Pb.$$

Notes. Impurities, such as iron, copper, cadmium, etc., in the acetate solution of lead seriously interfere in the chromate precipitation. These should be leached out with water containing a little sulphuric acid before extracting the lead sulphate with ammonium acetate.

[1] The yellow precipitate gives high results, since it is difficult to wash. The crystalline orange or red compound may be quickly filtered and washed.

### DETERMINATION OF LEAD AS THE MOLYBDATE, $PbMoO_4$

This method is rapid and has the following advantages:

*a*. The sulphation of lead is avoided. *b*. The acetate extraction is eliminated. *c*. The precipitate may be ignited. *d*. The ratio of lead to its molybdate compound is greater than either lead to $PbSO_4$ or to $PbCrO_4$, lessening the chance of error through weighing.

Cobalt, calcium, strontium and barium have little effect in presence of ammonium acetate. In absence of this salt they interfere slightly.

**Procedure.** — The ore or alloy is decomposed with nitric acid or aqua regia as the case may require. (Silica if present is eliminated by taking to dryness, dehydrating, taking up with dilute nitric acid and filtering.) To the clear liquid ammonium chloride is added and then sufficient ammonium oxalate to destroy the excess of free nitric acid.

Lead is now precipitated by adding 20 to 30 cc. of ammonium molybdate (4 grams per liter + acetic acid) stirring the mixture during the addition. After boiling for two or three minutes the precipitated lead molybdate is allowed to settle, then filtered through pulp, washed with small portions of hot water and ignited over a Bunsen burner.

The cooled residue is weighed as $PbMoO_4$. $PbMoO_4 \times 0.5642 = Pb$.

Notes. If antimony or other members of the group are present in the original sample it is advisable to dissolve the residue in HCl and reprecipitate the lead with molybdate reagent.

If lead is in the form of the sulphide, as may be the case in a complete analysis of a substance, it is decomposed with hot dilute $HNO_3$ and precipitated as $PbMoO_4$.

### Electrolytic Determination of Lead as the Peroxide, $PbO_2$

An electric current passed through a solution of lead containing sufficient free nitric acid will deposit all the lead on the anode as lead peroxide. The method is excellent for analysis of lead alloys. If copper is present it will be deposited on the cathode.

**Procedure.** — The sample containing not over 0.5 gram of lead is brought into solution by heating with dilute nitric acid, 1:1. The solution is washed into a large platinum dish with unpolished inner surface. Twenty to 25 cc. of concentrated nitric acid (sp.gr. 1.4) are added and the solution diluted to about 150 cc.

The sample is electrolyzed in the cold with 0.5 to 1 ampere current and 2 to 2.5 volts, the platinum dish forming the anode of the circuit, a spiral platinum wire or a platinum crucible dipped into the solution being the cathode. Three hours are generally sufficient for the deposition of 0.5 gram of Pb. Overnight is advisable, a current of 0.05 ampere being used.

A rapid deposition of the lead may be obtained by heating the solution to 60 to 65° C. and electrolyzing with a current $ND_{100}$ = 1.5 to 1.7 amperes, the E.M.F. varying within wide limits. Stirring the solution with a rotating cathode aids in the rapid deposition of the $PbO_2$.

To ascertain whether all the lead has been removed from the solution, more water is added so as to cover a fresh portion of the dish with water. The electrolysis is complete if no fresh deposition takes place after half an hour.

The water is siphoned off while more water is being added until the acid is removed, the current is then broken, the dish emptied of water and the deposits dried at 180° C. and weighed as $PbO_2$.

The deposit of lead peroxide gently ignited forms lead oxide, PbO.

$$PbO_2 \times 0.8662 = Pb. \quad PbO \times 0.9283 = Pb.$$

The deposits of lead oxide or peroxide may be removed by dissolving off with warm dilute nitric acid.

## VOLUMETRIC METHODS FOR DETERMINING LEAD

### THE CHROMATE-IODIDE METHOD FOR THE VOLUMETRIC DETERMINATION OF LEAD

The method depends upon the action of chromates on potassium iodide with a resulting liberation of an amount of free iodine in direct ratio to the chromate present, which in turn is a measure of the amount of lead isolated as lead chromate. The liberated iodine is determined by titration with a standard solution of thiosulphate. The discussion of the reactions that take place, with equations, are given in the notes that follow the directions of the method.

#### Solutions Required

**Sodium Acetate Extraction Solution.** — A saturated solution of sodium acetate, filtered to remove foreign matter if present, is diluted with twice its volume of distilled water and 30 cc. of 80 per cent acetic acid is added per liter of solution.

**Hydrochloric Acid Mixture.** — To a liter of saturated salt solution, filtered if necessary, is added 150 cc. of distilled water and 100 cc. of concentrated hydrochloric acid.

**Potassium Dichromate.** — Saturated solution, filtered if not clear.

**Starch Solution.**

**Procedure.** — 1. *Solution of the Sample.* Half a gram of the finely divided material, (if the factor weight 0.6907 g. is taken 1 cc. N/10 reagent in final titration is equivalent to about 1.% Pb) is dissolved in a beaker or a flask (Low's type) by adding 20 cc. of strong hydrochloric acid and heating gently until the action subsides. If the decomposition is incomplete about 5 cc. of nitric acid are added and the heating continued.

2. About 5 cc. of sulphuric acid are added and the solution evaporated to strong fumes. After cooling about 50 cc. of water are added and the solution is boiled to dissolve the soluble salts. If the ore is low grade 5–10 cc. of ethyl alcohol are now added, the precipitate is allowed to settled and then washed by decantation three or four times with 1 : 15 sulphuric acid (i.e. about 10% solution), and finally transferred to the filter with the dilute acid and washed once with pure cold water.

3. By means of a fine jet from a wash bottle (500 cc.) filled with sodium acetate extraction reagent, heated to near boiling the precipitate is transferred to the beaker or flask in which the precipitation was made. This may be done by carefully spreading out the filter in the funnel or by breaking the filter and washing the paper free of the lead sulphate with a fine stream of the reagent. If the precipitate does not go into solution more of the acetate is added and

heat gently applied until it dissolves. The solution is now diluted to 150 cc., heated to boiling and 10 cc. of the saturated dichromate solution added and the boiling continued ten minutes. The yellow color of the lead chromate precipitate changes to red. This is important to obtain a precipitate of definite composition.

4. The precipitate is filtered, the containing vessel washed out with hot dilute sodium acetate wash solution (50 cc. of the extraction solution diluted to 1000 cc.) and the precipitate washed ten times with the reagent.

5. The original beaker or flask is now placed under the funnel and the lead chromate is dissolved on the filter by adding cold dilute hydrochloric acid mixture, stirring up the precipitate with a jet of the reagent, adding the acid until all of the chromate has dissolved and the color has been completely removed from the filter. At least 50 cc. of the reagent should be used.

6. For low grade ores the entire solution is taken and treated with potassium iodide solution; in case of high grade ores, about half the solution is set aside in reserve, and upon completing the titration of the first portion, the reserve is added and the titration completed. This precaution is taken because a loss of iodine is apt to occur if much iodine is liberated at one time, free iodine being apt to escape as vapor from the easily saturated solution. (The solution is a poor solvent of iodine). To the solution are added 5 cc. of 25% potassium iodide and the liberated iodine is titrated with N/10 sodium thiosulphate until the iodine color begins to fade; starch solution is now added in sufficient quantity to produce a distinct blue color and the titration continued until the blue color changes to pale green.

A background of white assists in recognition of the end-point. A sheet of white paper placed under the beaker will do, if the base of the stand is not already white.

**Standardization of the Thiosulphate.** — This is best standardized against metallic lead. 0.6907 gram of pure lead should require 100 cc. of N/10 thiosulphate. 0.2 gram of lead is taken or a fraction of the factor weight (0.6907). The lead foil is dissolved in dilute nitric acid, (1 : 2), the nitric acid expelled by taking to fumes with 5 cc. of sulphuric acid, and the residue taken up with water and treated exactly according to the method outlined in steps 2–6 of the regular procedure. 1 cc. of N/10 thiosulphate is equivalent approximately to 0.0069 gram of lead.

Standardization against permanganate or dichromate — see the chapter on preparation of Reagents.

Notes. — If barium is present in the sample, the residue left from the acetate extraction may contain lead. This is treated with about 10 cc. of strong hydrochloric acid, evaporated to dryness, 25 cc. of the acetate reagent added, the mixture boiled, filtered and the residue washed. The filtrate contains the lead that remained with the residue.

In considering the reactions that take place it must be remembered that it

is the combined chromate radical that is responsible for the liberated iodine. (See Introduction § 25). The graphical formulae represent what takes place:

(*a*) $K_2Cr_2O_7$ (or $K_2O.Cr_2O_3.3O$) + 6KI = $3K_2O$ + 6I.

(*b*) $2K_2CrO_4$ (or $(K_2O).Cr_2O_3.3O$) + 6KI = $3K_2O$ + 6I.

(*c*) $2PbCrO_4$ (or $(PbO)_2.Cr_2O_3.3O$) + 6KI = $3K_2O$ + 6I.

It is evident that Pb is equivalent to 3 I. Therefore a normal equivalent of Pb is $\frac{1}{3}$ of its atomic weight, 207.2 divided by 3 = 69.07, hence 1 cc. of a N/10 solution will titrate iodine equivalent to .006907 g. Pb.

Since Fe equivalent is 55.84, Fe to Pb = 69.07 divided by 55.84 = 1.237.

*Reactions.*

(*a*) $2Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = 2PbCrO_4 + 2KC_2H_3O_2 + 2HC_2H_3O_2$.

(*b*) $2PbCrO_4 + 6KI + 16HCl = 2PbCl_2 + 6KCl + 2CrCl_3 + 8H_2O + 6I$.

(*c*) $6I + 6Na_2S_2O_3 = 6NaI + 3Na_2S_4O_6$.

### Volumetric Determination of Lead by the Molybdate Method

Lead is precipitated as molybdate from an acetic acid solution by a standard molybdic solution, the termination of the reaction being recognized by the yellow color produced by the excess of molybdic reagent when a drop of the mixture comes in contact with a drop of tannin solution used as an outside indicator.

## THE PERMANGANATE METHOD FOR LEAD [1]

**Procedure.** — Decompose 0.5 gram of the ore in an 8 oz., pear-shaped flask. See Introduction ¶ 24, page 42. The treatment may usually be a very gentle boiling with 10 cc. of hydrochloric acid for a short time, then adding 5 cc. of nitric acid and continuing the gentle boiling until decomposition is complete. Now add 6 cc. of sulphuric acid and boil over a free flame to strong fumes. Allow to cool.

Add 100 cc. of cold water and 5 cc. of sulphuric acid and heat to boiling. Remove from the heat, add 10 cc. of alcohol (cautiously) and cool under the tap.

Fold a 9 cm. filter with particular care to creasing the fold that will come next to the precipitate as thin as possible, so that it will lie flat and not easily allow material to get under the edge. Filter the mixture through this. Return the first portions of the filtrate if not clear. Wash six times with cold water containing 10% of alcohol. Any trace of lead sulphate remaining in the flask will be recovered subsequently.

With a jet of hot water, using as little as possible, rinse the precipitate from the filter, through a short funnel, back into the flask. (In the known or assumed presence of barium, interpolate the following short procedure: Add 10 cc. of hydrochloric acid and boil over a free flame almost to dryness. Allow to cool, add 20 cc. of water and a few drops of ammonia, sufficient to neutralize the acid.) Place the flask again under the original funnel and pour through the filter 10 cc. of a cold saturated solution of ammonium carbonate. Remove the flask and heat the contents just to boiling, then cool completely under the tap. Pour the cold mixture through the original filter. Wash out the flask well with cold water, pouring through the filter, and then wash filter and precipitate ten times with cold water containing about 5% of the ammonium carbonate solution. Reject the filtrate.

Again using a jet of hot water, wash the precipitate from the filter into a small beaker. Add 5–6 cc. of glacial acetic acid and heat to boiling. Replace the flask under the funnel and pour the hot acid mixture through the filter. Wash out the beaker with hot water and then wash the filter 10 times with hot water slightly acidulated with acetic acid. (Small amounts of lead carbonate may be dissolved directly upon the filter.)

Add to the filtrate 10 cc. of a cold saturated solution of oxalic acid, heat to boiling and then cool completely under the tap. Be particular to get as cold as possible. Now filter the lead oxalate through a 9-cm. filter. Using cold water, wash out the flask thoroughly and then wash the precipitate ten times.

Place about 25 cc. of cold water in the flask, add 5–6 cc. of sulphuric acid and then about 100 cc. of hot water. Drop the filter

[1] By Albert H. Low, Colorado School of Mines.

and precipitate into this. Wipe out any lead oxalate adhering to the funnel with a small piece of dry filter paper and drop into the flask. Heat the acid mixture nearly to boiling and then titrate it with standard potassium permanganate solution to a faint pink tinge. Calculate the result from the known lead value of the permanganate.[1]

[1] Theoretically, 1.857 times the iron factor will give the lead factor. Owing to slight losses of lead an empirical factor must be used. This is 1.879 times the iron factor. The permanganate may be standardized directly on lead as follows: Convert about 0.250 gram of pure lead foil to sulphate by boiling with 6 cc. of sulphuric acid. Continue according to the above entire process. Finally, divide the percentage value of the lead taken by the cc. of permanganate required, to obtain the percentage value of 1 cc. in lead.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Analysis of Metallic Lead

**Determination of Impurities in Pig Lead — Complete Analysis.**[1] — The following substances are generally estimated in the complete analysis of lead: silver, bismuth, copper, cadmium, arsenic, antimony, tin, iron, cobalt, nickel, manganese and zinc.

**Determination of Silver.** — This is determined by assay of 100 grams of lead. The substance is placed in a 3 in. scorifier and heated in a muffle furnace until the assay "covers." It is then poured into a mould, allowed to cool and the button thus obtained again scorified until a final button weighing about 20 grams is obtained. This is cupeled and silver determined as usual. If the silver bead is large it should be parted for gold.

**Determination of Bismuth.** — In determining bismuth three cases arise. *A*. The ordinary method. *B*. Procedure for determining minute amounts of bismuth. *C*. Method in presence of comparatively large amounts of antimony and tin.

*A*. Twenty grams of lead are dissolved in 100 cc. of hot dilute nitric acid (1:4). If the solution is complete, dilute ammonium hydroxide is added, drop by drop, until a faint opalescence is observed in the solution. If a precipitate is formed, this must be dissolved by addition of nitric acid and the ammonia treatment repeated. Now 5 cc. of dilute hydrochloric acid are added (1:9) and the solution diluted to 400 cc. and heated to boiling. The bismuth oxy-chloride is allowed to settle on the steam bath for several hours, the clear solution is then decanted through a 7 cm. filter (medium grade), the precipitate transferred to the paper and washed with hot water. (The solution is refiltered if cloudy.) The precipitate is dissolved with 5 cc. of hot hydrochloric acid (1:9), the acid being added around the edge of the filter with a pipette. The paper is washed and the solution diluted to 400 cc. and brought to boiling. The precipitate is filtered into a weighed Gooch crucible, washed several times with water, then once with alcohol and finally with ether. It is dried in the oven and weighed as BiOCl.

$$\mathrm{BiOCl} \times .802 = \mathrm{Bi}.$$

*B*. Determination of minute amounts of bismuth is made as follows: 100 grams of lead are dissolved in 500 cc. of dilute nitric acid (1:4), and the cooled solution treated with sufficient saturated solution of sodium carbonate to produce a heavy precipitate. After settling, then decanting off the clear solution, the precipitate is filtered onto a filter and drained. Without washing, this is dissolved with the

[1] Method of the National Lead Company, modified.

least amount of nitric acid that is required. The solution is then neutralized with ammonia as before (method *A*), litmus paper being used as an indicator, and bismuth determined as directed under the first procedure.

*C.* In presence of considerable amounts of antimony and tin, the bismuth is precipitated as in case *A*, the precipitate dissolved in hot hydrochloric acid (1 : 2), and the solution diluted to 200 cc. The sulphides of antimony, tin, etc., are precipitated with $H_2S$, antimony and tin dissolved out with a solution of potassium hydroxide and sulphide water (1 part of 20% KOH to 4 parts of $H_2S$ water), and the residue washed. This is dissolved in 20 cc. of hot nitric acid (1 : 4), and bismuth determined as usual in the filtrate.

**Determination of the Remaining Elements.** — 222.23 grams of the sample of lead are dissolved in 1100 cc. of dilute nitric acid (1 : 4) in a large beaker. If the solution is turbid, appreciable amounts of antimony and tin are indicated with possible sulphur combined as $PbSO_4$. In this case it is filtered into a 2000 cc. flask. If the solution is clear it is transferred directly to the flask.

**Residue I.** May contain As, Sb, Sn, $PbSO_4$.

**Filtrate I.** Contains all the elements present in the sample.

**Residue I.** — The residue and filter is treated with 20 cc. of tartaric acid mixture (50 grams of tartaric acid, 250 cc. of water and 250 cc. of concentrated hydrochloric acid). After boiling, the mixture is digested on the steam bath for half an hour, then 50 cc. of hot water added and the solution filtered. The filter paper is ignited and any residue is dissolved by fusion with 1 gram of potassium hydroxide in a silver dish. The water extract of this fusion is added to the tartrate solution. Now ammonia is added until the solution is alkaline and then hydrochloric acid until it is slightly acid. Hydrogen sulphide is now passed in to saturation, the precipitate digested on the steam bath for fifteen to twenty minutes and hydrogen sulphide again passed into the solution about fifteen minutes. The sulphides are filtered off, arsenic, antimony and tin sulphides dissolved with 5 cc. (1 : 5) potassium hydroxide in 25 cc. of saturated $H_2S$ water. The solution is diluted to 111 cc., and 100 cc. — equivalent to 200 grams of sample — preserved for subsequent analysis. This solution is marked "Extract C."

**Filtrate I.** — This solution, containing practically all of the material, is treated with 150 cc. of dilute sulphuric acid (1 : 1), and the solution made to volume — 2000 cc. It is now transferred to a 3 liter flask, the graduated flask rinsed out into the main solution with 50 cc. of water. (The $PbSO_4$ precipitate is found to occupy space of 50 cc.) When the precipitate has settled, 1800 cc. are decanted off. This represents 200 grams of the sample. The solution is boiled down in a No. 9 porcelain evaporating dish, heating first over the free flame and finally on the steam bath until only a moist residue remains.

Fifty cc. of water is added, the residue transferred to a beaker and digested for several hours, preferably overnight, and then filtered.

| **Residue II.** This may contain $PbSO_4$, As, Sb, Sn salts. | **Filtrate II.** This may contain Cu, Bi, Cd, Sn, Sb, As, Fe, Co, Ni and Zn. |
|---|---|

**Residue II.** — This is treated as has been described for residue I. The entire solution is added to the Extract C. The residue, consisting of $PbSO_4$, is rejected.

**Filtrate II.** — This is made neutral with ammonium hydroxide and then concentrated hydrochloric acid added in such an amount that the solution will contain 4% of free acid. (HCl, sp.gr. 1.2, 4 cc. per 100 of solution.) Hydrogen sulphide is now passed into the hot solution until it is saturated, the precipitate settled on the steam bath for half an hour and hydrogen sulphide again passed in for fifteen minutes. The precipitate is filtered off and washed with $H_2S$ water slightly acidified with hydrochloric acid.

| **Residue III.** May contain CuS, $Bi_2S_3$, CdS, $As_2S_3$, $Sb_2S_3$, SnS. | **Filtrate III.** May contain ions of Fe, Al, Co, Ni, Mn and Zn. This filtrate is marked " B." |
|---|---|

**Residue III.** — The sulphides are extracted with potassium hydroxide and hydrogen sulphide solution. This dissolves out arsenic, antimony and tin. This extract is combined with the extract marked " C."

The residue remaining is marked " Residue A."

The constituents of the sample have now been isolated in the groups.

**Residue " A "** contains the sulphides of copper, bismuth and cadmium.

**Filtrate " B "** contains such elements as do not precipitate as sulphides in acid solution — iron, aluminum, manganese, cobalt, nickel and zinc.

**Extract " C "** includes the elements arsenic, antimony and tin.

### Determination of Arsenic, Antimony, and Tin in Pig Lead

The combined alkali sulphide solutions: " Extract C " is washed into a beaker and acidified with 20 cc. of nitric acid and 5 cc. of hydrochloric acid. The solution is evaporated to dryness on the steam bath. The residue is dissolved in 200 cc. of water and 10 grams of oxalic acid added, together with 10 grams of ammonium oxalate, and the solution heated until clear.

Hydrogen sulphide gas is now passed into the hot solution for forty-five minutes.

**Precipitate.** $As_2S_3$,$Sb_2S_3$. **Filtrate** contains Sn.

**Arsenic.** — The precipitate containing arsenic and antimony is placed in a distilling flask, strong hydrochloric acid added and arsenic separated from antimony by distillation with a current of HCl gas according to the regular procedure. If a precipitate of arsenic sulphide forms in the distillate, it is advisable to precipitate the arsenic as sulphide, oxidize the compound to form sulphate and arsenic acid and after reduction of the arsenic to titrate it with standard iodine. This oxidation may be accomplished before distillation with hydrochloric acid. For details of the procedure see chapter on Arsenic.

**Antimony** is determined in the residue in the flask by titration with N/10 potassium bromate or by the potassium iodide method.

I. $2KBrO_3 + 2HCl + 3Sb_2O_3 = 2KCl + 2HBr + 3Sb_2O_5$.

II. (*a*) $Sb_2Cl_5 + 2KI = Sb_2Cl_3 + 2KCl + I_2$.
(*b*) $I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$.

For details of the procedure see chapter on Antimony.

### Determination of Copper and Cadmium in Pig Lead

The residue "A" is taken for this analysis. If copper exceeds 0.0025% method I is used. If the copper percentage is below this amount the procedure II is followed.

**Method I.** The residue is dissolved by heating with 20 cc. of nitric acid (1:4) and the solution filtered into a beaker. The filter is ignited and the residue dissolved in nitric acid (1:1) and the solution added to the first portion. The volume should not exceed 100 cc. Ammonium hydroxide is added until the solution is strongly ammoniacal and then 5 grams of potassium cyanide. Hydrogen sulphide is passed into the cold solution to saturation, and the solution filtered.

**Precipitate** = AgS, $Bi_2S_3$, CdS. **Filtrate** = Cu in solution.

The filtrate containing the copper is evaporated on the steam bath to a volume of 20 to 30 cc. in a 4 in. casserole. Now 20 cc. of sulphuric acid (1 : 1) are added (hood), and the solution evaporated until $SO_3$ fumes are evolved. The cooled concentrate is diluted with water and filtered, if necessary. Three cc. of nitric acid are added per 100 cc. of solution and the copper deposited by electrolysis according to the regular procedure and weighed as metallic copper. For detailed method see chapter on Copper.

The precipitate containing silver, bismuth and cadmium is dissolved in 20 cc. of nitric acid (1:4), 1 cc. of 1% sodium chloride solution is added, the solution digested half an hour and then filtered and the filter washed with water.

**Precipitate — AgCl,** reject. **Filtrate — $Cd(NO_3)_2$ and Bi $(NO_3)_3$.**

The filtrate is made slightly alkaline with sodium carbonate added in slight excess, and 5 grams of potassium cyanide are then added. After digesting on the steam bath for half an hour the solution is filtered and the residue washed with 5% sodium carbonate solution.

**Precipitate** contains bismuth, reject.

**Filtrate** contains cadmium.

The filtrate is now treated with a few cc. of ammonium sulphide and the yellow cadmium sulphide is filtered into a weighed Gooch crucible, then washed, dried and finally weighed as CdS.

$$CdS \times 0.778 = Cd.$$

**Method II.** — Small amounts of copper. The filter containing the sulphides is ignited in a porcelain crucible and the residue dissolved in 5 to 10 cc. of nitric acid (1 : 1), and the solution evaporated to pastiness. One cc. of sulphuric acid (1 : 1) is added together with a few drops of 10% sodium chloride solution and the mixture evaporated to $SO_3$ fumes, the cooled product then diluted with water and filtered from the lead and silver precipitates.

Ammonia is now added to the filtrate together with 5 grams of potassium cyanide and CdS and $Bi_2S_3$ are precipitated with $H_2S$, as in case I, and filtered off.

**Precipitate — CdS and $Bi_2S_3$.** Bismuth is removed as before and cadmium sulphide again precipitated and the compound titrated with N/10 iodine solution.
1 cc. N/10 I = 0.00562 gram Cd.

**Filtrate.** The solution is made acid in the hood with $H_2SO_4$, then taken to $SO_3$ fumes and copper determined by the potassium iodide method.

### Determination of Iron, Cobalt, Nickel, Manganese and Zinc in Pig Lead

**Iron and Aluminum.** — The filtrate "B" from members of the Hydrogen Sulphide Group is evaporated to 100 cc. and the iron oxidized with a few drops of nitric acid as usual. Iron (and aluminum) hydroxide is now precipitated by addition of ammonia. It is advisable to dissolve this precipitate in hydrochloric acid and reprecipitate the iron to recover the occluded manganese and zinc. The combined filtrates are reserved for the determination of the remainder of the elements. The hydroxide of iron is ignited and weighed as $Fe_2O_3$. If alumina is suspected, the residue is dissolved in hydrochloric acid and iron determined volumetrically. $Fe_2O_3$ thus obtained is subtracted from

the weight of the first determination, the difference being due to the alumina present.

$Fe_2O_3 \times 0.6994 = Fe$ Reciprocal factor = 1.4298

$Al_2O_3 \times 0.5303 = Al$ Reciprocal factor = 1.8856

**Zinc.** — The filtrate from iron precipitate is made neutral with hydrochloric acid and then 15 drops of 2N. HCl added in excess and zinc precipitated in the pressure flask with $H_2S$. (See illustration in the chapter on Arsenic.) The sulphide of zinc is filtered off, and either ignited to the oxide ZnO and so weighed or determined by a volumetric procedure. See chapter on Zinc.

$ZnO \times 0.8034 = Zn.$
$H_2SO_4 \times 0.6665 = Zn.$

**Cobalt and Nickel.** — These are best determined by electrolysis, being deposited from an ammonium sulphate solution.

If a separation of the elements is desired the deposit is dissolved in acid, nickel determined by O. Brunck's dimethylglyoxime method, and cobalt determined by difference.

**Manganese.** — The solution from nickel and cobalt is taken to dryness, and the residue heated to expel the ammonium salts and destroy any organic matter present. This is taken up with a little hydrochloric acid, then 2 to 3 cc. of sulphuric acid added and the mixture evaporated to $SO_3$ fumes to expel the hydrochloric acid. When nearly all the free acid is driven off, the moist residue, cooled, is treated with 50 cc. of nitric acid (1 : 3), and manganese determined in the solution preferably by the bismuthate method. For minute amounts of manganese the colorimetric procedure is used. See chapter on Manganese.

## DETERMINATION OF LEAD PEROXIDE IN MINIUM (RED LEAD)

Lead peroxide is reduced by oxalic acid according to the reaction:

$$PbO_2 + H_2C_2O_4 = PbO + 2CO_2 + H_2O.$$

The peroxide reduced by an excess of oxalic acid is determined by titrating this excess with standard potassium permanganate.

**Procedure.** — About 0.2 g. of minium is heated with 25 cc. of 2N $HNO_3$ (one volume of $HNO_3$, sp.gr. 1.2, to two volumes of $H_2O$) and then 50 cc. of N/5 oxalic acid added. The solution is heated to boiling and the excess oxalic acid titrated with N/5 potassium permanganate. 1 cc. of N/5 $KMnO_4$ = .0239 g. $PbO_2$.

## DETERMINATION OF SMALL AMOUNTS OF LEAD

The determination of minute quantities of lead is required in baking powders, canned goods and like products in which small amounts of lead are objectionable. Traces of lead ranging from 5 to 100 parts per million (0.0005 to 0.01% Pb) are best determined colorimetrically on 0.5 to 1 gram samples; larger amounts of lead should be determined gravimetrically.

### Gravimetric Methods for Determining Traces of Lead

The determination of extremely small amounts of lead cannot be accomplished by the usual methods of precipitation, as the lead compounds remain in solution in a colloidal state. The addition, however, of certain substances, which form amorphous precipitates with the reagents used for throwing out lead causes the removal of lead from the solution by occlusion.

### Precipitation of Lead by Occlusion with Iron Hydroxide

Wilkie found that ferric hydroxide has the property of occluding lead, five parts of $Fe(OH)_3$ removing one part of lead from solution. Advantage is taken of this property of iron hydroxide in precipitating small amounts of lead.

**Procedure.** — The required amount of material is weighed out in 50 gram lots and brushed into No. 8 beakers. If the material contains organic matter, it is treated with 200 cc. portions of concentrated hydrochloric acid, the mixture heated just below the boiling-point of HCl solution, and potassium chlorate added, a few crystals at a time, until the organic matter is decomposed (hood). If the material dissolves in water, the water solution is treated with 5 cc. of concentrated hydrochloric acid and a few crystals of potassium chlorate and the liquor boiled.

**Addition of Ferric Iron.** — If sufficient iron is not already present, ferric chloride is added in such quantity that the iron content of the sample will be from twenty to fifty times that of the lead (larger amounts of iron will do no harm) present in the solution. Five to 10 cc. of concentrated nitric acid are added and the sample boiled for ten to fifteen minutes.

**Precipitation of Iron and Lead.** — If alumina is present, iron is precipitated by addition of a large excess of potassium hydroxide, the alumina going into solution as potassium aluminate. In absence of alumina, ammonia may by used to precipitate the ferric hydroxide. Lead is completely occluded by the precipitate and carried down. The solution is filtered hot through large size rapid filters, threefold.

The filtering must be done quickly and the liquid kept hot to prevent clogging of the filters.

**Separation of Lead from Iron.** — The precipitate is dissolved in hot hydrochloric acid (free from lead). The solutions are combined, if several portions of the sample are taken. Concentrated sulphuric acid is added and the sample evaporated to small volume and heated until the white sulphuric acid fumes appear. The usual procedure is now followed for separation of the lead sulphate, acetate extraction of lead and final precipitation of lead chromate.

$$PbCrO_4 \times 0.641 = Pb.$$

NOTE. In place of using alcohol to decrease the solubility of lead sulphate, many prefer to add sulphuric acid so that the acidity of the solution will be 2–10% of free $H_2SO_4$.

## COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF LEAD

Estimation of small amounts of lead by the intensity of the brown coloration produced by the sulphide in colloidal solution and comparison with a standard solution is the principle of this method. Details of the method are given in the author's work — Standard Methods of Chemical Analysis.

### DIRECTIONS FOR THE USE OF A DUBOSCQ TYPE OF COLORIMETER

The mirror is turned so that the two halves of the field appear to be equally illuminated with the cups clean and empty. The solutions are then poured into the cups. The cup containing the standard solution is then lowered to a definite thickness of the standard solution between the bottom of the cup and the end of the plunger. With this movement the half of the field corresponding to the standard solution is seen to darken, while the other half remains luminous and colorless. If the cup containing the unknown solution is now moved in its turn, the two halves of the field are brought to the same intensity, after which the height at which the two liquid columns display this equal absorptive power is read by means of this scale. The proportion of coloring matter in two solutions is inversely proportional to the heights of the two columns necessary to obtain the same intensity of illumination, thus if the standard tube is set at 10 mm., and the solution under examination is the same intensity of color at 20 mm., the latter is just one-half the concentration of the standard. This is usually expressed by the formula:

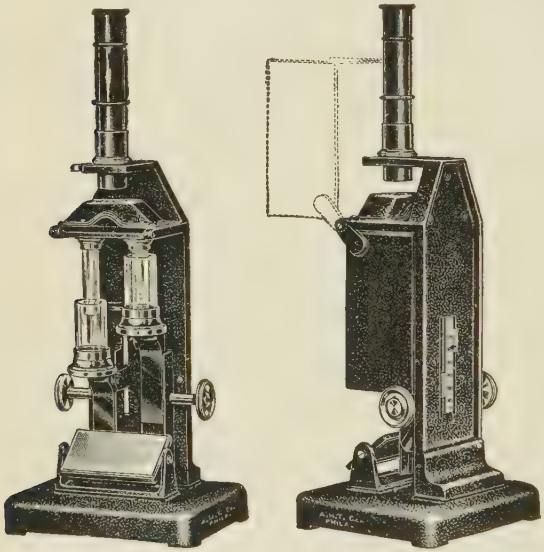


Fig. 86. — Colorimeter.
By courtesy of the Arthur H. Thomas Company, Philadelphia, Pa.

$$\frac{\textit{Color of test solution}}{\textit{Color of standard solution}} = \frac{\textit{Height of standard solution}}{\textit{Height of solution to be tested}}$$

If, therefore, the scale reading is 20 mm. for the standard, and 15 mm. for the solution to be tested, the formula reads: $\frac{20}{15} = 1.33$.
If, for example, the standard solution contains 4 cc. of coloring matter in 100 cc., the solution under test will be found to contain $4 \times 1.33 = 5.32$ cc. in 100 cc.

## MAGNESIUM

**Mg, at.wt. 24.32; sp.gr. 1.69–1.75; m.p. 651°; b.p. 1120° C.; oxide MgO.**

The element is determined in the complete analysis of a large number of substances; in the analysis of ores, minerals, rocks, soils, cements, water, etc.

### OCCURRENCE

The element occurs combined only in nature, a large number of minerals being known. It is found in sea water and in certain mineral waters. It occurs as a phosphate and carbonate in the vegetable and animal kingdoms especially in seeds and bones. The following are the more important minerals of magnesium:

**Minerals.** *Dolomite*, Pearl Spar, Magnesian Limestone, $MgCO_3.CaCO_3$.

*Brucite*, $Mg(OH)_2$, white or gray, translucent foliated masses with wax-like lustre, sectile and flexible; white streak; hardness 2.5.

*Magnesite*, $MgCO_3$, white, brittle, dense rounded nodules, or coarse grained, brittle; opaque to translucent; dull vitreous or silky; white streak; hardness 3.5–4.5.

Other minerals of magnesium — Carnallite, $KCl.MgCl_2.6H_2O$; Spinel, $MgO.Al_2O_3$; Pyroxene, Ca, Mg etc. silicate; Pyrope, $Mg_3Al_2(SiO_4)_3$; Amphibole, Ca, Mg etc. silicate; Chrysolite, $(Mg, Fe)_2SiO_4$; Biotite, Mg, Fe mica; Phlogopite, Mg mica; Clinochlore, Penninite, $H_8Mg_5Al_2Si_3O_{18}$; Serpentine, $H_4Mg_3Si_2O_9$; Talc, $H_2Mg_3(SiO_3)_4$; Boracite, $Mg_7Cl_2B_{16}O_{30}$; Kieserite, $MgSO_4.H_2O$; Epsomite, $MgSO_4.7H_2O$; Hypersthene; Anthophyllite; Glaucophane; Iolite; Chondrodite; Sepiolite, etc.

### DETECTION

In the usual course of analysis magnesium is found in the filtrate from the precipitated carbonates of barium, calcium, and strontium. The general procedure for removal of the preceding groups may be found in Separations. Magnesium is precipitated as white magnesium ammonium phosphate, $MgNH_4PO_4$, by an alkali phosphate, $Na_2HPO_4$, $NaNH_4HPO_4$, etc., in presence of ammonium chloride and free ammonia. The precipitate forms slowly in dilute solution. This is hastened by agitation and by rubbing the sides of the beaker during the stirring with a glass rod. Crystals soon appear on the sides of the beaker in the path of contact, and finally in the solution.

**Baryta or lime water** added to a solution containing magnesium produces a white precipitate of magnesium hydroxide.

Both the phosphate and the hydroxide of magnesium are soluble in acids.

*The alkali bicarbonates* or acid carbonates, $NaHCO_3$, $KHCO_3$ do not precipitate magnesium but on boiling the solution and elimination of $CO_2$ the carbonate $MgCO_3$ precipitates.

Magnesium is a powerful reducer and liberates a large number of the elements from their oxides when the metal is heated with these, Ag, Hg, Pt, Sn, B, Al, Th, C, Si, Pb, P, As, Sb, Bi, Cr, Mo, Mn, Fe, Co, Ni, Cu, Cd, Zn, Gl, Ba, Sr, Ca, Rb, K, Na, Li. (Prescott and Johnson — Qual. Chem. Anal.)

## METHODS FOR THE DETERMINATION OF MAGNESIUM

### Preparation and Solution of the Sample

In solution of the material it will be recalled that the metal is soluble in acids and is also attacked by the acid alkali carbonates. It is soluble in ammonium salts. The oxide, hydroxide, and the salts of magnesium are soluble in acids. Combined in silicates, however, the substance requires fusion with alkali carbonates to bring it into solution.

**General Procedure for Ores.** — One gram of the ore is treated with 20 cc. of strong hydrochloric acid and heated gently until the material is decomposed. If sulphides are present, 5 to 10 cc. of strong nitric acid are added and the material decomposed by the mixed acids. If silicates are present and the decomposition is not complete by the acid treatment, the insoluble material is decomposed by fusion with sodium carbonate, or the entire sample may be fused with the alkali carbonate, the fusion is dissolved in hydrochloric acid and taken to dryness. Silica is dehydrated as usual by heating the residue from the evaporated solution. This is taken up with 50 cc. of water containing about 5 cc. of strong hydrochloric acid, the silica filtered off, and, after removal of the interfering substances according to procedures following, the magnesium is determined.

**Alloys.** — Solution may be effected by treating the alloy with nitric acid followed by hydrochloric acid. The alloys of magnesium are generally soluble in the mineral acids, hydrochloric, nitric or sulphuric acid.

**Salts.** — Solution frequently may be accomplished in distilled water. Should the salt not dissolve readily in water, addition of a little hydrochloric acid will bring it into solution.

**Removal of Members of the Hydrogen Sulphide Group. Copper, Lead, Bismuth, Cadmium, Arsenic, etc.** — The filtrate from silica is diluted to about 200 cc. and hydrogen sulphide gas passed in until the members of this group are completely precipitated. The sulphides are filtered off and washed with $H_2S$ water and the filtrate and washings concentrated by boiling. This treatment is seldom necessary in analysis of many silicates and carbonates in which these elements are absent.

**Removal of Iron, Aluminum, Manganese, Zinc, etc.** — The concentrated filtrate from the hydrogen sulphide group, or in case the treatment with hydrogen sulphide was not required, the filtrate from silica, is boiled with a few cc. of nitric acid to oxidize the iron (solution turns yellow), about 5 cc. of concentrated hydrochloric acid added, and if manganese is present, 15 to 20 cc. of a saturated solution of bromine water, and the solution made alkaline to precipitate iron, aluminum, manganese. If zinc, cobalt, and nickel are present, these

are best removed as sulphides by passing hydrogen sulphide into the ammoniacal solution preferably under pressure.

**Separation of Magnesium from the Alkaline Earths.** — The alkaline earths are precipitated either as oxalates, recommended when considerable calcium is present, or as sulphates, recommended in presence of a large proportion of barium, the magnesium salts being soluble. Magnesium is precipitated from the filtrates as a phosphate, according to directions given later. Details of the separation of magnesium from the alkaline earths may be found in the chapter on Barium.

## HINTS FOR THE STUDENT

For practice in the determination of magnesium dissolve 1 gram of a soluble magnesium salt in 100 cc. of distilled water and add 1–2 grams of ammonium chloride or its equivalent in solution. Now follow directions given under the gravimetric method for determination of magnesium. The magnesium precipitate may be transferred from the beaker to the filter by means of the filtrate poured back into the beaker; loss due to solubility is thus prevented.

## GRAVIMETRIC DETERMINATION OF MAGNESIUM

### Precipitation of Magnesium by a Soluble Phosphate as Ammonium Magnesium Phosphate

Magnesium is determined in the filtrate from calcium oxalate by the addition of sodium ammonium phosphate to a hot slightly acid or neutral solution followed by a definite amount of ammonia. The practice of precipitating magnesium from a cold solution necessitates a double precipitation as the composition of the phosphate is considerably modified by that of the solution in which the precipitation takes place, so that it is necessary to adjust conditions by having a definite amount of ammonia, ammonium salts and phosphate for the approximate amount of magnesium present. Accurate results are obtained by precipitation of the compound from a hot solution by the method of B. Schmitz, by addition of the soluble phosphate to a slightly acid solution and then making ammoniacal, or that of W. Gibbs, by precipitation of the amorphous magnesium hydrogen phosphate in a neutral solution and transforming the precipitate to magnesium ammonium phosphate by addition of ammonia to the hot solution. Upon ignition of the precipitate, magnesium pyrophosphate ($Mg_2P_2O_7$) is formed.

**Reactions.**

*A*. $Na_2NH_4PO_4 + MgCl_2 = 2NaCl + MgNH_4PO_4$ (B. Schmitz).

*B*. $NaNH_4HPO_4 + MgCl_2 = NaCl + NH_4Cl + MgHPO_4$ and

$MgHPO_4 + NH_3 = MgNH_4PO_4$ (W. Gibbs).

Decomposition with Heat.

$$2MgNH_4PO_4 = 2NH_3 + H_2O + Mg_2P_2O_7.$$

**Reagents.** — *Sodium ammonium phosphate, $NaNH_4HPO_4$* or disodium phosphate. (The former is preferred.)

Ammonium hydroxide, ammonium chloride, hydrochloric acid.

**Procedure.** — 1. The metals of the previous groups having been removed, the solution (diluted to about 150 cc.) containing magnesium in presence of ammonium salts, is neutralized (litmus paper test) and made slightly acid with 2–3 drops of hydrochloric acid, and then heated to boiling. Now treat as follows.

2. To the hot solution add drop by drop, sufficient sodium ammonium phosphate reagent to completely precipitate the magnesia and half again as much excess. 1 cc. of a 10% $NaNH_4HPO_4.4H_2O$ solution will precipitate 0.116 gram of Mg. so that 15 cc. of the reagent

should be ample for a 1 gram sample. Stir the solution during the addition but do not scrape walls of beaker with stirring rod.[1]

3. Make an approximate measurement of the volume of the solution and add to the hot solution one-third its volume of dilute ammonia (sp.gr. 0.96, dilution 1:3).

4. Stir thoroughly and allow to settle for about two hours, the solution cooling to room temperature. Longer standing will do no harm.

5. Filter, decanting off the clear solution, and wash the precipitate by decantation two or three times with dilute ammonia water (1000 cc. of $H_2O$ with 25 cc. of $NH_4OH$). 2% solution of ammonium nitrate may be used in place of ammonium hydroxide. Transfer the precipitate to the filter and wash free of chlorides, (4–5 additional washings) using the ammonia solution.

6. Dry the precipitate and remove from the filter paper, placing it in a weighed porcelain crucible. Ignite the filter and add its ash to the precipitate. Now ignite the precipitate over a low flame for 5–10 minutes, increase the heat until the precipitate is at red heat. Now blast over a Meker burner or heat in an electric oven for 15–30 minutes, or until the weight is constant.

7. The residue will be snow white if the oxidation of the carbon and the ignition has been properly conducted. Cool and weigh as $Mg_2P_2O_7$.

Factors. $Mg_2P_2O_7 \times 0.3621 = MgO$ or $\times 0.2184 = Mg$ or $\times 0.7572 = MgCO_3$ or $\times 1.0811 = MgSO_4$ or $\times 2.2143 = MgSO_4.7H_2O$.

### Notes on Magnesium

In place of using filter paper the magnesium ammonium phosphate precipitate is filtered into a weighed Gooch crucible and ignited, after gently heating for a few minutes until the water and $NH_3$ has been expelled. This lessens the difficulty with occluded carbon in the precipitate as is apt to occur when filter paper is used.

The ignition is conducted gently at first to gradually oxidize the carbon that the precipitate contains. With rapid ignition the particles are inclosed in the mass in a form that it is almost impossible to completely oxidize, so that the final residue is gray instead of white. L. L. de Koninck considers that the blackening of the precipitate is frequently due to the presence of organic bases in commercial ammonia and its salts, rather than to the fibers of filter paper occluded in the mass. With caution, the filter and residue may be ignited wet, the heat being low until the filter completely chars and then being increased, with the cover removed, until the residue is white. Incomplete washing may also cause carbon occlusion by the easily fusible microcosmic salt or sodium phosphate that remains with the magnesium salt.

Large amounts of ammonium salts may form $Mg(NH_4)_4PO_4$ which requires prolonged heating to convert it to $Mg_2P_2O_7$.

**Impurities.** — The precipitate may contain traces of lime that remained soluble in ammonium oxalate. This may be determined by dissolving the

[1] The magnesium salt would adhere firmly to the walls of the beaker where the rod scratched the sides.

pyrophosphate in dilute sulphuric acid followed by addition of 9 to 10 volumes of absolute alcohol. Calcium sulphate, $CaSO_4$, precipitates and settles out on standing several hours. It may be filtered off, dissolved in hydrochloric acid and precipitated as oxalate in the usual way and so determined.

A residue remaining after treating the pyrophosphate with acid is generally $SiO_2$.

The presence of manganese may be detected by dissolving the magnesium pyro-phosphate, $Mg_2P_2O_7$, in nitric acid and oxidizing with sodium bismuthate. (See method under Manganese.)

**Properties of Ammonium Magnesium Phosphate.** — Readily soluble in dilute acids. One hundred cc. of pure water at 10° C. will dissolve 0.0065 gram. The presence of ammonia greatly decreases the solubility of the salt, e.g., 2.5% ammonia decreases the solubility to 0.00006 gram of MgO per 100 cc. The presence of ammonium salts increases the solubility of the precipitate, e. g., 1 gram of ammonium chloride will increase the solubility to 0.0013 gram of MgO.

## VOLUMETRIC DETERMINATION OF MAGNESIUM

### Titration of the Ammonium Magnesium Phosphate with Standard Acid

The procedure known as Handy's volumetric method for magnesium, depends upon the reaction $MgNH_4PO_4 + H_2SO_4 = MgSO_4 + NH_4H_2PO_4$. An excess of standard sulphuric acid is added to the precipitate and the excess of acid titrated back with standard ammonium hydroxide.

**Procedure.** — The method of precipitation of the magnesium ammonium phosphate is the same as has been described under the gravimetric method. The precipitate is washed several times by decantation with 10% ammonium hydroxide solution (1 part $NH_4OH$, sp.gr. 0.90 to 9 parts water), and finally on the filter. After draining, the filter is opened out, the moisture removed as much as possible by means of dry filter papers. The residue may be dried in the room for about forty-five minutes or in the air oven at 50 to 60° C. for fifteen to twenty minutes. When the filter has dried, ammonia will have been expelled. The substance is placed in a dry beaker, N/10 sulphuric acid added in excess (methyl orange indicator), the solution diluted to 100 cc. and the excess of acid titrated with N/10 sodium hydroxide.

One cc. N/10 of $H_2SO_4$=0.002 gram. of MgO.

## MANGANESE

**Mn, at.wt. 54.93; sp.gr. 7.42; m.p. 1260°; b.p. 1900° C.; oxides, MnO, $Mn_2O_3$, $Mn_3O_4$ ignition in air, $MnO_2$, $MnO_3$, $Mn_2O_7$.**

Manganese may be determined accurately gravimetrically or volumetrically. The former methods may be used for high-grade manganese ores, the latter are generally preferred for determining manganese in steel and in alloys and are applicable to a wide range of substances. Manganese is determined in its ores for their evaluation. It is determined in alloys. Speigeleisen or ferromanganese is an important alloy for the steel industry. In addition to the requirement of the element in the analysis of the above substances it is determined in certain paint pigments — green and violet manganous oxides, in dryers of oils, etc.

### OCCURRENCE

Manganese occurs native only in meteorites, combined it is found in a number of minerals. Traces are found in animals and plants.

**Minerals.** — Among the more important minerals are:

*Braunite*, $3Mn_2O_3.MnSiO_3$, brownish-black, opaque, brittle mineral; granular masses or minute tetragonal pyramids; submetallic; streak like color; hardness 6–6.5.

*Pyrolusite*, Black Oxide of Manganese, $MnO_2$, a soft black, opaque, rather brittle mineral; compact, massive, velvety crusts or short radiated crystals; metallic to dull lustre; streak like color; hardness 1–2.5.

*Manganite*, $Mn_2O_3.H_2O$, an opaque, brittle, steel gray to iron black mineral with submetallic lustre occurring in short or long prismatic, orthorhombic crystals often in bundles, rarely massive, granular or stalactitic. Streak reddish-brown to black; hardness 4.

*Rhodochrosite*, $MnCO_3$, light pink, rose-red to brownish-red or brown, brittle, transparent to opaque mineral with vitreous lustre; white streak; hardness 3.5–4.5.

**Other minerals.** – Franklinite, $(Fe.Zn.Mn)O\ (Fe,Mn)_2O_3$; Rhodonite, $MnSiO_3$, Columbite-Tantalite, $(Fe,Mn)\ (Nb\ Ta)_2O_6$; Psilomelane, $MnO_2 + H_2O$, $K_2O$ or BaO, or $H + MnO_5$; Alabandite, MnS, Hausmannite, $Mn_3O_4$, Wad-Bog Manganese; Tephroite $Mn_2SiO_4$ etc.

### SUGGESTION TO STUDENTS

Determine Manganese in Steel or in an ore by the Bismuthate or Oxalic Acid Method. See pages 374–380.

### DETECTION

In the usual course of analysis manganese is found in the filtrate from the hydroxides of iron, aluminum and chromium, the previous groups having been removed with hydrochloric acid, hydrogen sulphide and ammonium hydroxide in presence of ammonium chloride. Manganese, cobalt, nickel and zinc are precipitated as sulphides in an ammoniacal solution. The sulphides of manganese and zinc are dissolved by cold dilute hydrochloric acid, $H_2S$ expelled by boiling and manganese precipitated as the hydroxide by addition of potassium hydroxide in sufficient amount to dissolve the zinc (sodium zincate). Manganese is now confirmed by dissolving this precipitate in nitric acid and adding red lead or lead peroxide to the strong nitric acid solution. A violet-colored solution is produced in presence of manganese. Chlorides should be absent.

**Manganese in soils, minerals, vegetables, etc.,** is detected by incinerating the substance, treating the ash with nitric acid and taking to dryness; the residue is taken up with water and the mixture filtered. To the filtrate is added a few cc. of 40% ammonium persulphate and a little 2% silver nitrate solution. A pink color is produced in presence of manganese.

**Manganese compounds heated with borax** in the oxidizing flame produce an amethyst red color. The color is destroyed in the reducing flame.

**Fused with sodium carbonate and nitrate** on a platinum foil manganese compounds produce a green-colored fusion ("robin egg blue").

## METHODS FOR THE DETERMINATION OF MANGANESE

### Preparation and Solution of the Sample

In dissolving the sample the following facts will be recalled: The metal dissolves in dilute acids, forming manganese salts. The oxides and hydroxides of manganese are soluble in hot hydrochloric acid. Manganous oxide is soluble in nitric or in sulphuric acid; the dioxide is insoluble in dilute or concentrated nitric acid, but is soluble in hot concentrated sulphuric acid.

**Ores of Manganese.** — A sample of powdered ore weighing 1 gram is brought into solution by digesting with 25 to 50 cc. of strong hydrochloric acid for fifteen to thirty minutes on the steam bath. If much silica is present 5 to 10 cc. of hydrofluoric acid will assist solution. If sulphides are present add 5 cc. of nitric acid. Five cc. of sulphuric acid are added and the mixture evaporated and heated until fumes of sulphur trioxide are evolved. The residue is taken up with a little water and warmed until the sulphates have dissolved. If decomposition is incomplete and a colored residue remains, this is filtered off, ignited in a platinum dish and fused with a little potassium bisulphate. The fusion is dissolved in water containing a little nitric acid and the solution added to the bulk of the sample.

If manganese is to be determined volumetrically the removal of iron is not necessary. If, however, a gravimetric procedure is to be followed, iron and alumina are removed by the basic acetate method given under separations and manganese precipitated in the filtrate. In presence of small amounts of iron and alumina, precipitation with ammonia in presence of ammonium chloride will remove these elements without appreciable loss of manganese, a double precipitation being usually advisable. For volumetric procedures in ores containing over 2% manganese an aliquot portion of the sample is taken for the determination. The portion should not contain over 0.01 gram of manganese.

**Alloys. Manganese Alloys.** — One gram of ferromanganese is dissolved in 50 cc. of dilute nitric acid (sp.gr. 1.135) and oxidized with sodium bismuthate with boiling. The cooled solution is diluted to 500 cc. and 10 to 25 cc. is treated with about 30 cc. of dilute nitric acid and manganese determined by the bismuthate method. The amount of sample taken is governed by the manganese content. This should not exceed 0.01 gram of the element if the volumetric procedure is to be followed.

**Separation of Manganese from Interfering Elements.** — As is frequently the case, isolation of manganese is not necessary, since it may be determined volumetrically in presence of a number of elements, which would interfere in its gravimetric determination. The analyst should be sufficiently familiar with the material to avoid

needless manipulations, which not only waste time, but frequently lead to inaccurate results.

**Removal of Elements of the Hydrogen Sulphide Group.** — This separation may be required in the analysis of certain alloys where a separation of manganese from copper is required.

The acid solution containing about 4% of free hydrochloric acid (sp.gr. 1.2), is saturated with hydrogen sulphide and the sulphides filtered off. Manganese passes into the filtrate. This treatment will effect a separation of manganese from mercury, lead, bismuth, cadmium, copper, arsenic, antimony, tin and the less common elements of the group.

**Separation of Manganese from the Alkaline Earths and the Alkalies.** — The separation is occasionally required in the analysis of clays, limestone, dolomite, etc. It is required in the complete analysis of ores. In the usual course of a complete analysis of a substance, the filtrate from the hydrogen sulphide group is boiled free of $H_2S$ and is treated with a few cc. of nitric acid to oxidize the iron. The solution is made slightly ammoniacal with ammonia, in presence of ammonium chloride, whereby iron, aluminum and chromium are precipitated as hydroxides. The filtrate is treated with hydrogen sulphide or colorless ammonium sulphide, whereby manganese, nickel, cobalt and zinc are thrown out as sulphides and the alkaline earths and alkalies remain in solution.

### Separation of Manganese from Iron and Aluminum, Basic Acetate Method

The procedure effects a separation of iron, aluminum, titanium, zirconium and vanadium from manganese, zinc, cobalt and nickel.

The separation depends upon the fact that solutions of acetates of iron, aluminum, titanium, zirconium and vanadium are decomposed when heated and the insoluble basic acetates precipitated, whereas the acetates of manganese, zinc, cobalt and nickel remain undecomposed when boiled for a short time.

$$Fe(C_2H_3O_2)_3 + 2HOH = 2HC_2H_3O_2 + Fe(OH)_2.C_2H_3O_2.$$

The solvent action of the liberated acetic acid is prevented by the addition of sodium acetate which checks ionization of the acid. The method requires care and is somewhat tedious, but the results attained are excellent.

**Procedure.** — To the cooled acid solution of the chlorides is added a concentrated aqueous solution of sodium carbonate from a burette with constant stirring until the precipitate that forms dissolves slowly. A dilute solution of the carbonate is now added until a slight permanent opalescence is obtained. With the weak reagent and careful addition of the carbonate drop by drop the proper neutralization of

the free acid is obtained. With considerable iron present the solution appears a dark red color, fading to colorless as the quantity of iron decreases to a mere trace in the solution. Three cc. of acetic acid (sp.gr. 1.044) are added to dissolve the slight precipitate. The more perfect the neutralization before heating the less amount of reagent required for precipitating iron — an excess of reagent does no harm. If this does not clear the solution in two minutes, more acetic acid is added a drop at a time until the solution clears, allowing a minute or so for the reaction to take place with each addition. The solution is diluted to about 500 cc. and heated to boiling and 6 cc. of a 30% sodium acetate solution added. The solution is boiled for one minute and removed from the flame. (Longer boiling will form a gelatinous precipitate, difficult to wash and filter.) The precipitate is allowed to settle for a minute or so, then filtered, while the liquid is hot, through a rapid filter and washed with hot, 5% sodium acetate solution three times. The apex of the filter is punctured with a glass stirring rod and the precipitate washed into the original beaker in which the precipitation was made with a fine stream of hot, 1:1 hydrochloric acid solution from a wash bottle. (Dilute $HNO_3$ may be used in place of HCl.)

**A second precipitation** with neutralization of the acid and addition of sodium acetate is made exactly as directed above. It is advisable to evaporate the solution to small volume to expel most of the free mineral acid before addition of $Na_2CO_3$ to avoid large quantities of this reagent. The filtrates contain manganese, zinc, cobalt and nickel; the precipitate iron, aluminum, titanium, zirconium, vanadium.

### Separation of Manganese as the Dioxide, $MnO_2$

The procedure is of special value in the complete analysis of ores where a basic acetate separation of iron and aluminum has been made, and a gravimetric estimation of other constituents in the solution are desired.

The procedure depends upon the principle that manganese in a dilute solution of manganous salt is oxidized to manganese dioxide and so precipitated, when boiled with bromine or certain other oxidizing agents:

$$MnCl_2 + Br_2 + 2H_2O = MnO_2 + 2HCl + 2HBr.$$

The free acid formed by the reaction must be neutralized either by ammonia or by the presence of a salt of a weak acid such as sodium acetate, otherwise the precipitation of manganese will be incomplete. In presence of ammonium acetate much of the bromine is used up reacting with ammonia,

$$MnCl_2 + Br_2 + 4NH_4C_2H_3O_2 + 2H_2O = MnO_2 + 2NH_4Cl + 2NH_4Br + 4HC_2H_3O_2.$$

At the same time acetic acid is formed, which does not decompose the oxide. It is necessary to have sufficient acetate present to prevent resolution of the manganese.

**Procedure.** — To the solution containing manganese is added 4 to 5 grams of sodium acetate (unless already present in excess), the solution being diluted to about 200 cc. Bromine water is added until a distinct color of bromine is evident. The mixture is boiled and kept boiling for ten to fifteen minutes, additional bromine being added in small portions. The precipitate is allowed to settle and filtered off. The filtrate is boiled with additional bromine to ascertain whether the manganese has been completely removed from the solution.

If ammonia is present, as is frequently the case, it is advisable to add more of the reagent from time to time, the solution having a distinct odor of ammonia after the last portion of bromine has been added. When large amounts of manganese are present, several separations may be required to remove the element from the subsequent filtrates.

The precipitated dioxide may be dissolved in sulphuric acid and manganese determined volumetrically or gravimetrically.

It may be ignited directly and weighed as $Mn_3O_4$.

It may be evaporated with sulphuric acid and manganese determined as $MnSO_4$.

Manganates of zinc or calcium will be precipitated if present in large amounts.

Manganese may also be precipitated by ammonium persulphate in an ammoniacal solution, by potassium chlorate and hypochlorite of lime in presence of zinc chloride in a neutral solution.

## GRAVIMETRIC METHOD

### DETERMINATION OF MANGANESE AS PYROPHOSPHATE

Manganese is precipitated as ammonium manganese phosphate, $NH_4MnPO_4$, and then ignited to pyrophosphate, $Mn_2P_2O_7$. The method is known as Gibbs' Phosphate Process.[1]

**Procedure.** — The cold solution of manganese chloride[2] obtained as directed in previous sections, should be diluted so as to contain not over 0.1 gram of manganese oxide equivalent per 100 cc. of solution. A cold saturated solution of ammonium sodium hydrogen phosphate (microcosmic salt, 170 grams per liter; 9 cc. precipitates an equivalent of 0.1 gram of the oxide) is now added in slight excess. The solution is made strongly ammoniacal and heated to boiling, the boiling being continued until the precipitate becomes crystalline. After allowing to settle until cold, the precipitate is filtered off (the filtrate being tested with more of the precipitating reagent to assure that an excess had been added), and dissolved in a little dilute hydrochloric or sulphuric acid.

Reprecipitation of the phosphate. The free acid is neutralized with ammonia added in slight excess until the odor is quite distinct, the solution heated to boiling, and a few cc. of additional phosphate reagent added. The crystalline precipitate is filtered into a weighed Gooch crucible, washed free of chlorides with very dilute ammonia ($AgNO_3 + HNO_3$ test), dried and ignited to the pyrophosphate. The ignition is conducted, as in case of magnesium, by heating first over a low flame and gradually increasing the heat to the full power of the burner. The final residue will appear white or a pale pink.

$$Mn_2P_2O_7 \times 0.4996 = MnO,$$

$$Mn_2P_2O_7 \times 0.3869 = Mn.$$

Notes. Zinc, nickel, copper and other elements precipitated as phosphates should be absent from the solution. The separation from iron is generally made by the basic acetate method and manganese precipitated from the filtrate, free of other elements, as the peroxide $MnO_2$, by means of bromine added to the ammoniacal solution. Other oxidizing reagents may be used, as has been stated. The dioxide is dissolved in strong hydrochloric acid and the above precipitation effected.

[1] Gibbs' C.N., 17, 195, 1868.

[2] Some analysts prefer to add the phosphate reagent to the strongly ammoniacal solution, boiling hot.

## VOLUMETRIC METHODS

### BISMUTHATE METHOD FOR DETERMINATION OF MANGANESE

The method is based on the fact that a manganous salt in the presence of an excess of nitric acid is oxidized to permanganic acid by bismuth tetroxide. The permanganic acid formed is very stable in nitric acid of 1.135 sp.gr., when the solution is cold, but in hot solutions the excess of the bismuth tetroxide is rapidly decomposed, and then the nitric acid reacts with the permanganic acid, and, as soon as a small amount of manganous salt is formed, the remainder of the permanganic acid is decomposed, manganous nitrate dissolves, and manganese dioxide precipitates. The method is especially applicable for determining small amounts of manganese.

**Solutions Required.** — *Nitric Acid* (1 : 3): Mix 250 cc. of $HNO_3$ sp.gr. 1.42, and 750 cc. of distilled water.

*Nitric Acid for Washing:* Mix 30 cc. of $HNO_3$ sp.gr. 1.42 and 970 cc. of distilled water.

*Ferrous Ammonium Sulphate:* Dissolve 12.4 g. of ferrous ammonium sulphate crystals in 950 cc. of distilled water, and add 50 cc. of $H_2SO_4$ sp.gr. 1.84.

*Potassium Permanganate:* Dissolve 1 g. of $KMnO_4$ in 1000 cc. of distilled water. Allow it to stand for about one week and then filter it through asbestos. Standardize against 0.10 g. portions of pure sodium oxalate.

**Method.** — In a 250 cc. Erlenmeyer flask dissolve 1 g. of the metal containing manganese in 50 cc. of $HNO_3$ (1 : 3). Without filtering off the residue, cool and add 0.5 g. of sodium bismuthate. Heat for a few minutes until the purple color has disappeared, with or without the precipitation of manganese dioxide. Add a little ferrous-ammonium sulphate solution until the solution becomes clear, and boil until the oxides of nitrogen are expelled. Cool, add an excess of sodium bismuthate and agitate for a few minutes. Add 50 cc. of $HNO_3$ for washing and filter through an alundum crucible or an asbestos pad. Wash with 50 cc. of the $HNO_3$ for washing. Add from a pipette or a burette 10 cc. of ferrous ammonium sulphate solution and titrate with $KMnO_4$. In copper alloys, owing to the presence of considerable copper, the end-point is somewhat different from the normal pink color.

In exactly the same manner carry through a blank determination, using the same amounts of $HNO_3$ and sodium bismuthate as was done with the regular sample. Finally add exactly 10 cc. of ferrous-ammonium sulphate solution and titrate with $KMnO_4$. The difference between the two titrations is due to the manganese. Since one manganese as permanganate oxidized five irons, the iron value of the permanganate multiplied by the factor (Mn/5 Fe) (or 0.1967) gives the value in terms of manganese.

*Accuracy:* Duplicate determinations should check within 0.02 per cent of manganese.

NOTES. Instead of employing the method of reducing the permanganic acid by means of standardized ferrous ammonium sulphate solution and titrating the excess of this reagent, it is possible to reduce the permanganic acid by standard sodium arsenite solution.

The filtrate from the bismuthate must be perfectly clear, as the least particle of bismuthate carried into the filtrate will vitiate the results.

NOTE. In the analysis of white irons it may be necessary to treat the solution several times with bismuthate to destroy the combined carbon. The solution, when cold, should be nearly colorless; if not, another treatment with bismuthate is necessary.

## Notes and Precautions

**Special Steels.** — Steels containing chromium offer no special difficulties, except that it must be noted that while in hot solutions the chromium is oxidized to chromic acid, which is reduced by the addition of sulphurous acid, the oxidation proceeds so slowly in cold solutions that if there is no delay in the filtration and titration the results are not affected. Steels containing tungsten are sometimes troublesome on account of the necessity for getting rid of the tungstic acid. Those that decompose readily in nitric acid may be filtered and the filtrate treated like pig iron, but when it is necessary to use hydrochloric acid it is best to treat with aqua regia, evaporate to dryness, redissolve in in hydrochloric acid, add a few drops of nitric acid, dilute, boil, and filter. Get rid of every trace of hydrochloric acid by repeated evaporations with nitric acid, and proceed as with an ordinary steel.

The delicacy of the reaction of manganese in nitric acid solution with sodium bismuthate is extraordinary; 0.000005 gram of manganese gave an appreciable color in 50 cc. of solution.

As will be seen in the description of the various methods of solution, the use of hydrochloric acid has been avoided, because the presence of even traces of this reagent is fatal to the accuracy of the method. Where it is impossible to avoid its use, and its presence is suspected in the final nitric acid solution, the addition of a drop or two of silver nitrate will overcome the difficulty, but the filter must be rejected after using it for filtering a solution so treated.

Any form of asbestos filtering tube may be used for filtering off bismuthate, but the perforated cone with bell jar is the most satisfactory, because it has the largest area of filtering service. One filter may be used for fifty or more determinations, and the time occupied in filtering and washing one determination is only from one minute and a half to three minutes. The filtrate must be clear, for the least particle of bismuthate carried through will vitiate the result by reacting with the excess of ferrous sulphate. As soon as the filtration and washing are completed, the ferrous sulphate should be added, and the excess titrated with the permanganate solution, as the permanganic acid gradually decomposes on standing, and the warmer the solution the more rapid is the decomposition. At a temperature of 5° C. the solution will remain unaltered for several hours, but at 40° C., fifteen minutes will show an appreciable change. The larger the amount of manganese the more rapid the change.

It is especially important not to allow the solution to stand after adding the ferrous sulphate, as the excess of this reagent reacts with the nitric acid in a few minutes and the formation of the smallest amount of nitrous oxide is fatal to the accuracy of the determination. For this reason it is important to boil off every trace of nitrous oxide when, in the earlier part of the operation, sulphurous acid or other deoxidizing agent is added.

When working with steels of unknown manganese content, it may often happen that 25 cc. of ferrous sulphate solution are insufficient to entirely re-

duce the permanganic acid, in which case an additional amount of ferrous sulphate must be added. It will be noticed that the solution of permanganic acid upon the addition of an insufficient amount of ferrous sulphate does not necessarily retain its pink or purple color, but usually changes to a dirty brown. When this occurs 10 cc. more of ferrous sulphate is added to the flask and the value of the two additions taken as the amount from which the number of cc. of permanganate, corresponding to the excess of ferrous sulphate, must be subtracted. When the sample is low in manganese, the 10 cc. ferrous sulphate alone may be used.

There is no advantage in using permanganate solutions differing in strength from the one given above, but the strength of the ferrous sulphate solution may be changed to meet special cases.

### Oxidation of Manganese to Permanganate by Red Lead

Red lead oxidizes manganese in nitric acid solution to permanganate. The method is suitable for determining this element in steel and iron in presence of molybdenum, aluminum, tungsten, copper and nickel, in amounts such as are apt to be present. The method is given in the chapter on Iron in the Analysis of Iron and Steel.

### VOLHARDS' METHOD FOR MANGANESE HIGH GRADE PRODUCTS.[1]

The method is based on the principle that when potassium permanganate is added to a neutral manganese salt all of the manganese is oxidized and precipitated. When this stage is reached any excess of permanganate is immediately evident by the color produced. The calculation of results may be based on the reaction,

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4,$$

or $$5ZnSO_4 + 6MnSO_4 + 4KMnO_4 + 14H_2O = 4KHSO_4 + 7H_2SO_4 + 5ZnH_2.2MnO_3,$$

the ratio in either case being $2KMnO_4 = 3Mn$.

**Procedure.** — The material decomposed with hydrochloric and nitric acid and taken to fumes with sulphuric acid, as stated for the preparation of the sample, is cooled and boiled with 25 cc. of water until the anhydrous ferric sulphate has dissolved. Then continue as follows:

**Removal of Iron.** — Transfer the mixture to a 500 cc. graduated flask and add an emulsion of zinc oxide in slight excess to precipitate the iron (C.P. $ZnSO_4$ precipitated by KOH added to slight alkalinity. The washed precipitate is kept in a stoppered bottle with sufficient water to form an emulsion). Agitate the flask to facilitate the precipitation and see that a slight excess of zinc oxide remains when the reaction is complete. Now dilute the contents of the flask up to the mark with cold water, mix thoroughly and allow to stand a short time and partially settle.

**Titration.** — By means of a graduated pipette draw off 100 cc. of the clear supernatant liquid and transfer it to an 8 oz. flask. Heat the solution in the small flask to boiling, add two or three drops of nitric acid (which causes the subsequent precipitate to settle more quickly) and titrate with a standard solution of potassium permanganate.

The permanganate causes a precipitate which clouds the liquid and it is therefore necessary to titrate cautiously and agitate the flask after each addition, and then allow the precipitate to settle sufficiently to observe whether or not the solution is colored pink. A little experience will enable one to judge by the volume of the precipitate formed, about how rapidly to run in the permanganate. The final pink tinge, indicating the end of the reaction, is best observed by holding the flask against a white background and observing the upper edges of the liquid.

When this point is attained, bring the contents of the flask nearly to boiling and again observe if the pink tint still persists, adding more permanganate if necessary.

[1] The method *is not* recommended for low grade ores.

In making this end test avoid actually boiling the liquid, as a continual destruction of the color may sometimes thus be effected and the true end-point considerably passed. When the color thus remains permanent the operation is ended. Observe the number of cc. of permanganate solution used and calculate the result.

From the equation above it is evident that 1 cc. N/10 of $KMnO_4$ titrates .001648 g. Mn (i.e. $\frac{\text{at.wt. Mn} \times 3}{10 \times 1000} = .001648$)

The iron value of the $KMnO_4$ reagent multiplied by 0.2952 = Mn equivalent.

## AMMONIUM PERSULPHATE METHOD FOR DETERMINING SMALL AMOUNTS OF MANGANESE BY COLORIMETRIC COMPARISON OR BY TITRATION

The process depends upon the oxidation of manganous salts to permanganate by ammonium persulphate in presence of a catalytic agent such as silver nitrate:

$$2Mn(NO_3)_2 + 5(NH_4)_2S_2O_8 + 8H_2O = 5(NH_4)_2SO_4 + 5H_2SO_4 + 4HNO_3 + 2HMnO_4.$$

The reaction takes place equally well in sulphuric or in nitric acid solution, or in a mixture of the two. The essential point is the presence of a sufficient amount of silver nitrate catalyst.

**Solutions Required.** — *Solution for Dissolving:* Mix 500 cc. of $H_2SO_4$, sp.gr. 1.84, 200 cc. of $HNO_3$ sp.gr. 1.42, and 1700 cc. of distilled water.

*Silver Nitrate:* Dissolve 1.33 g. of $AgNO_3$ in 1000 cc. of distilled water.

*Stock Sodium Arsenite:* To 15 g. of arsenious oxide ($As_2O_3$) in a 300 cc. Erlenmeyer flask, add 45 g. of $Na_2CO_3$ and 150 cc. of distilled water. Heat the flask and contents on the steam bath until the $As_2O_3$ is dissolved. Cool the solution, filter and make up to 1000 cc. with distilled water.

*Standard Sodium Arsenite:* Mix 200 cc. of stock sodium arsenite solution with 2500 cc. of distilled water, and standardize against a steel or iron of known manganese content as determined by the Bismuthate Method, or standardize against one of the Bureau of Standards' standard irons or steels. One cc. of this solution should be equivalent to approximately 0.00050 g. of manganese.

*Ammonium Persulphate:* Dissolve 60 g. of ammonium persulphate in 1000 cc. of distilled water.

**Procedure.** — One gram of ore is dissolved in hydrochloric acid, followed by sulphuric and taken to fumes as directed under Preparation and Solution of the Sample. The sulphate taken up with water is made to a volume of 100 cc. If the color comparison is to be made

the solution should be filtered through a dry filter, otherwise the filtration may be omitted. Twenty cc. (equal to 0.2 gram) of the material is taken for the test. In the case of steel, 0.1 to 0.2 gram of the drilling, dissolved in dilute nitric acid, is taken.

**Oxidation.** — The solution is transferred to a test-tube, 1 × 10 ins., if the color comparison is to be made, or into a 150-cc. Erlenmeyer flask, if the sample is to be titrated. Fifteen cc. of silver nitrate solution (1.5 grams $AgNO_3$ per liter of water) are added; the solution heated to 80 to 90° C. by placing the receptacle in hot water) and then 1 gram of ammonium persulphate added. When the color commences to develop the sample is cooled in cold water while the evolution of oxygen continues. The sample is poured into the comparison tube and the color compared with that obtained from an ore or steel sample of known manganese content, run in the same way.

In the titration method the solution in the Erlenmeyer flask is diluted to about 100 cc., 10 cc. of 0.2% salt solution added, and the sample titrated with standard sodium arsenite until the permanganate color is destroyed. The cc. of the reagent used multiplied by the factor per cc. in terms of manganese equals weight of manganese in the sample titrated.

NOTE. Arsenious acid reagent is made by dissolving 10 grams of arsenious oxide in water containing 30 grams of sodium carbonate. The solution is diluted to 1 liter. 125 cc. of this solution are diluted to 2000 cc. This latter reagent is standardized against an ore or sample of steel of known manganese content, following the directions given under the procedure outlined.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Analysis of Spiegel Iron for Manganese [1]

**Procedure.** — Weigh 0.5 gram of the sample in a 25 cc. beaker, add 40 cc. of dilute $HNO_3$ (1–2), cover with a watch-crystal, heat over a Bunsen burner and finally expel nitrous fumes by boiling down to a small volume (5 cc.).[2] Wash into a 500-cc. graduated flask, fill about half full, neutralize with an emulsion of zinc oxide, adding enough to precipitate the iron and a *slight* excess.[3] Dilute to the mark, shake well, pour into a 600 cc. beaker and mix by pouring back into the flask and then into beaker. Allow the precipitate to settle, decant off two 100 cc. portions of clear solution into 350 cc. casseroles. Add 100 cc. of water, heat to boiling and titrate with standard $KMnO_4$, stirring thoroughly with heavy glass rod. Run in about 1 cc. at a time until the end-point is passed.[4] Titrate the second portion, running it up to within 1 cc. of the end-point, and finishing a drop or two at a time, stirring thoroughly between each addition.[5] The burette reading gives percentage of Mn directly.

**Determination of Manganese in Ores, Oxalic Acid Method.** — The method is applicable for determining manganese in low and in high grade ores. Details are given as an example on page 72 of the introductory chapter.

[1] Procedure communicated to the author by Dr. Breyer.

[2] It is necessary to boil off nitrous fumes, as they will consume $KMnO_4$.

[3] Always test the zinc oxide for reducing substances.

[4] In samples in which the percentage of Mn is known approximately, almost the full amount of $KMnO_4$ can be added at once.

[5] Do not mistake the reflection of precipitated $MnO_2$ for excess of $KMnO_4$. If properly carried out the $MnO_2$ should collect in center of casserole.

## MERCURY

**Hg, at.wt. 200.6; sp.gr. 13.595; m.p.–38.9°; b.p. 357.33° C.; oxides, $Hg_2O$, HgO.**

### OCCURRENCE

The metal is found free in the upper portions of cinnabar deposits. As an amalgam with silver it occurs in horn silver. Cinnabar, HgS, is the only ore of mercury of commercial importance. The element has been found in quartz, sandstone, schists, iron pyrites, bituminous substances, eruptive and sedimentary rocks of all ages. It occurs in sulphide ores of other metals — especially in zinc ores.

**Minerals.** — *Native Mercury*, Hg, a tin white opaque liquid with metallic lustre, specific gravity 13.59. Found in globules scattered in the gangue, or in cavities with cinnabar or calomel.

Mercury volatilizes in the flame of the blowpipe. It is soluble in nitric acid.

*Cinnabar*, Natural Vermillion, HgS, a heavy, scarlet to reddish-brown, brittle to sectile mineral, opaque to transparent, adamantine to dull in lustre, red masses of granular texture, rarely small transparent rhombohedral crystals; sometimes nearly black from the presence of organic matter, carbon etc; streak scarlet; hardness 2–2.5.

*Calomel*, Horn Mercury, $Hg_2Cl_2$, a gray or brown translucent mineral; sectile; adamantine lustre; streak white; hardness 1–2. Usually found as a coating near cinnabar.

*Other minerals.* — Coloradoite, HgTe; Amalgam, (Ag, Hg); Livingstonite, $HgSb_4O_7$; Tiemannite, HgSe.

### DETECTION

Metallic mercury is recognized by its physical properties. It is the only metal which is a liquid at ordinary temperatures. The element forms a convex surface when placed on glass.

Mercury in the mercurous form is precipitated by hydrochloric acid as white mercurous chloride, HgCl. This compound is changed by ammonium hydroxide to the black precipitate of metallic mercury and nitrogen dihydrogen mercuric chloride. Mercuric mercury is precipitated as the black HgS from acid solution by $H_2S$ gas. The element is distinguished from the other members of the group by the insolubility of its sulphide in yellow ammonium sulphide and in dilute nitric acid.

If the mercury sulphide is dissolved in aqua regia, the nitric acid expelled by taking to dryness, and by adding hydrochloric acid and evaporating again to dryness, the residue then taken up with a little hydrochloric acid, water added and then a solution of stannous chloride, a white precipitate of mercurous chloride is first formed, which is further reduced to metallic mercury by an excess of the reagent. For quantitative methods it must be kept in mind that the chloride of mercury is slightly volatile. A complete loss occurs by prolonged heating.

## GRAVIMETRIC METHODS

### PREPARATION AND SOLUTION OF THE SAMPLE

Nitric acid is the best solvent for the metal. The oxides are insoluble in alkalies. Mercuric oxide is soluble in acids. Mercurous oxide, however, forms mercurous chloride, insoluble in dilute hydrochloric acid. Cinnabar, the important ore of mercury, may be decomposed by aqua regia or by sulphuric acid and crystals of potassium permanganate. The volatility of mercury salts necessitates careful evaporations of solutions. Prolonged heating of residues on the steam bath will cause loss of mercury.

### DETERMINATION OF MERCURY BY PRECIPITATION WITH AMMONIUM SULPHIDE

The following method, suggested by Volhard, is generally applicable for determination of mercury. The element is precipitated by ammonium sulphide as HgS. The precipitate dissolved in caustic is again thrown out by addition of ammonium nitrate to the sulpho salt solution of mercury.

$$Hg(SNa)_2 + 2NH_4NO_3 = 2NaNO_3 + (NH_4)_2S + HgS.$$

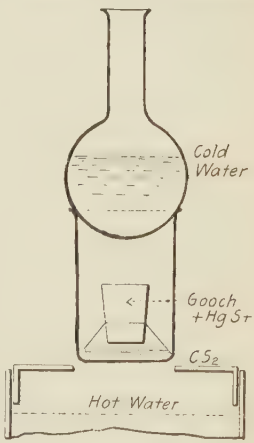


FIG. 87

**Procedure.** — The acid solution of the mercuric salt is nearly neutralized by sodium carbonate, and is then heated with a slight excess of ammonium sulphide reagent, freshly prepared. Sodium hydroxide solution is added until the dark-colored liquid begins to lighten. The solution is now heated to boiling and more sodium hydroxide added until the liquid is clear. If lead is present it will remain undissolved and should be filtered off. Ammonium nitrate is now added to the solution in excess and the mixture boiled until the greater part of the ammonia has been expelled. The clear liquid is decanted from the precipitate through a weighed Gooch crucible and the precipitate washed by decantation with hot water and finally transferred to the crucible and washed two or three times more. The mercuric sulphide is dried at 110° C. and weighed as HgS.

$$HgS \times 0.8622 = Hg \text{ or } \times 0.9307 = HgO.$$

NOTES. Alumina and silica are apt to be present in caustic.

Free sulphur may be removed, if present, by boiling with sodium sulphite, $Na_2SO_3 + S = Na_2S_2O_3$. The sulphur may be extracted with carbon disulphide. The Gooch crucible is placed upon a glass tripod in a beaker, containing carbon

disulphide, and a round-bottomed flask filled with cold water is placed over the mouth of the beaker to serve as a condenser, Fig. 87. By gently heating over a water bath for an hour the sulphur is completely extracted from the sulphide. Carbon disulphide is removed from the precipitate by washing once with alcohol followed by ether. The residue is now dried and weighed.

## DETERMINATION OF MERCURY BY ELECTROLYSIS

Mercury is readily deposited as a metal from slightly acid solutions of its salts.

**Procedure.** — The neutral or slightly acid solution of mercuric or mercurous salt is diluted in a beaker to 150 cc. with water and 2 to 3 cc. of nitric acid added. The solution is electrolyzed with a current of 0.5 to 0.1 ampere, and an E.M.F. of 3.5 to 5 volts. A gauze cathode is recommended, or a platinum dish with dulled inner surface may be used. One gram of mercury may be deposited in about fifteen hours (or overnight). The time may be shortened to about three hours by increasing the current to 0.6 to 1 ampere.

The metal is washed with water without interrupting the current and then with alcohol. After removing the adhering alcohol with a filter paper, the cathode is placed in a desiccator containing fused potash and a small dish of mercury. The object of this mercury is to prevent loss of the deposit by vaporization.

The increased weight of the cathode is due to metallic mercury.

Notes. In the electrolysis of mercuric chloride turbidity may be caused by formation of mercurous chloride by reduction, but this does no harm, as the reduction to metallic mercury follows.

Mercury may be electrolyzed from its sulpho solutions, obtained by dissolving its sulphide in concentrated sodium sulphide.

## DETERMINATION OF MERCURY BY THE HOLLOWAY-ESCHKA PROCESS MODIFIED

When mercury sulphide is heated with iron filings metallic mercury is volatilized, iron sulphide being formed. The mercury vapor is condensed on a silver or gold plate. The use of iron for this reduction was suggested by Eschka and his method modified by Holloway. In ores containing arsenic the addition of zinc oxide is recommended. Erdmann and Marchand use lime for decomposing the mercury compound. The reactions may be represented as follows:

$$Hgs + Fe = FeS + Hg \text{ or } HgX + CaO = CaX + Hg + O.$$

**Apparatus.** — This consists of a deep glazed porcelain crucible, the size depending upon the charge of the sample to be taken. Generally a 30-cc. crucible is used for a 2 gram sample with 4 grams of flux. The crucible is covered by a silver or gold plate that lies perfectly flat and fits snugly around the edges of the crucible. It may

be necessary to grind the top of the receptacle on emery paper to obtain a perfectly level edge.

The crucible is suspended in a hole through an asbestos board or quartz plate, to prevent the flame heating the upper portion of the vessel.

The lid of the crucible is kept cool by a cylindrical condenser of metal through which a stream of water passes. A small Erlenmeyer flask may be used, with a tube passing to the bottom of the flask through a rubber stopper, and a second tube just passing through the stopper.

Holloway has a weight placed on the metal condenser to hold the lid firmly against the crucible. The illustration (Fig. 88) shows the form of the apparatus set up for the run.

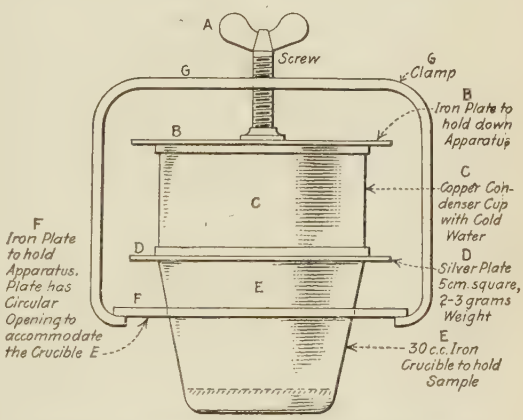



FIG. 88. — Apparatus for Determining Mercury.

**Procedure.** — The sample containing not over 0.1 gram of mercury is placed in the crucible with 5 to 10 grams of fine iron filings and intimately mixed. Additional filings are put over the charge. Sulphide ores containing arsenic are best mixed with about twice the weight of a flux of zinc oxide and sodium carbonate in the proportion 4 to 1, and about five times the weight of iron filings added.

The weighed silver cover is placed on the crucible and the apparatus set up as shown in the illustration, Fig. 88.

The bottom of the crucible is gradually heated with a small Méker flame until it glows slightly. Overheating should be avoided. The upper portion of the crucible should never become hot and the lid should remain cold. After heating for about thirty minutes the system is allowed to cool without disconnecting the condenser. The disk is now removed, dipped in alcohol and dried in a desiccator over fused potash or soda. The increase of weight of the dried disk is due to metallic mercury.

NOTES. If the sample contains less than 1 % mercury, take 2 grams; if 1 to 2 % mercury, take 1 gram; if the sample contains 2 to 5 %, take 0.5-gram sample. If high in mercury, grind sample with sand and take an aliquot portion.

It is advisable to repeat the test with a clean foil to be sure that all the mercury has been driven out of the sample. The foil may be freed from mercury by heating.

## VOLUMETRIC DETERMINATION OF MERCURY

### SEAMON'S VOLUMETRIC METHOD

**Seamon's Volumetric Method.** — Weigh 0.5 gram of the finely ground ore into an Erlenmeyer flask of 125 cc. capacity. Add 5 cc. of strong hydrochloric acid and allow it to act for about ten minutes at a temperature of about 40° C., then add 3 cc. of strong nitric acid and allow the action to continue for about ten minutes longer. The mercury should now all be in solution. Now if lead be present, add 5 cc. of strong sulphuric acid; it may be omitted otherwise. Dilute with 15 cc. of water and then add ammonia cautiously until the liquid is slightly alkaline. Bismuth, if present, will be precipitated. Acidify faintly with nitric acid, filter, receiving the filtrate in a beaker, and wash thoroughly.

Add to the filtrate 1 cc. of strong nitric acid that has been made brownish in color by exposure to the light, and titrate with a standard solution of potassium iodide until a drop of the liquid brought into contact with a drop of starch indicator, on a spot-plate, shows a faint bluish tinge. It is a good plan to set aside about one-third of the mercury solution and add it in portions until the end-point is successively passed, finally rinsing in the last portion and titrating to the end-point very carefully.

Deduct 0.5 cc. from the burette reading and multiply the remaining cc. used by the percentage value of 1 cc. in mercury to obtain the percentage in the ore.

The standard potassium iodide solution should contain 8.3 grams of the salt per liter. Standardize against pure mercuric chloride. Dissolve a weighed amount of the salt in water, add 2 cc. of the discolored nitric acid and titrate as above. One cc. of standard solution will be found equivalent to about 0.005 gram of mercury, or about 1% on the basis of 0.5 gram of ore taken for assay.

The precipitate of red mercuric iodide which forms during the titration may not appear if the amount of mercury present is very small, but this failure to precipitate does not appear to affect the result.

Iron, copper, bismuth, antimony, and arsenic, when added separately to the ore, did not influence the results in Seamon's tests. Silver interferes. Duplicate results should check within 0.1 to 0.2 of 1%.

## MOLYBDENUM

**Mo, at.wt. 96.0; sp.gr. 8.6–9.01; m.p. 2500° C.; oxides, $Mo_2O_3$, $MoO_2$, MoO.**

### OCCURRENCE

The commercial ores of molybdenum are molybdenite, the native sulphide ($MoS_2$), and wulfenite, lead molybdate. Occasionally molybdenum ochre (the trioxide) may be met with, but this mainly occurs in very small proportion associated with molybdenite as an oxidation product of the sulphide.

Molybdenite is sold either as high grade selected mineral or as concentrates which are usually the product of flotation processes. The important determinations in molybdenite are molybdenum, arsenic, copper and phosphorus; sometimes bismuth is present and occasionally lead.

Owing to the complex nature of wulfenite the determination of molybdenum is more difficult and the number of impurities which may be sought for is much greater. Some iron and copper ores also contain molybdenum.

The metal is determined in certain self-hardening steels and alloys.

The reagents ammonium molybdate and the molybdic acid, $MoO_3$, are valuable for analytical purposes. Tests of their purity may be required.

**Minerals.** — *Molybdenite*, $MoS_2$, a bluish gray, opaque, sectile to malleable mineral with metallic lustre, foliated masses or scales like graphite, easily separated; soft, marks paper; greenish streak; hardness 1–1.5. With blowpipe flame on charcoal $SO_2$ evolved, soluble in nitric acid and in sulphuric acid (blue solution) distinction from graphite, which it strongly resembles.

*Molybdite*, $MoO_3$, an earthy yellow powder, opaque to translucent; streak yellow; hardness 1–2.

*Wulfenite*, $PbMoO_4$, sometimes contains Ca, Cr, V, a yellow to orange-red, mineral with resinous lustre; hardness 3. Usually in thin, square, tetragonal crystals, occasionally in granular masses or acute pyramidal crystals.

### DETECTION

Molybdenum appears in the hydrogen sulphide group, being precipitated by $H_2S$ in acid solution as the sulphide. It passes into solution by digestion with ammonium sulphide or sodium sulphide along with arsenic,

antimony, tin, gold, and platinum. By addition of metallic zinc, antimony, together with tin, gold and platinum are precipitated as metals while molybdenum remains in solution. Arsenic that has not volatilized as arsine, is expelled by evaporation. Nitric acid is now added and the solution taken to dryness. Molybdenum is extracted from the residue with ammonium hydroxide.

A dilute solution of ammonium molybdate treated with a soluble sulphide gives a blue solution

**Sodium thiosulphate** added to a slightly acid solution of ammonium molybdate produces a blue precipitate with a supernatant blue solution. With more acid a brown precipitate is formed.

**Sulphur dioxide** produces a bluish-green precipitate if sufficient molybdenum is present, or a colored solution with small amounts. The reducing agents, stannous chloride, or zinc in acid solution, produce a play of colors when they react with molybdenum solutions, due to the formation of the lower oxides. The solution becomes blue, changing to green, brown and yellow.

Molybdenum present as molybdate is precipitated by *disodium phosphate* as yellow phosphomolybdate from a nitric acid solution. The precipitate is soluble in ammonium hydroxide.

A pinch of powdered mineral on a porcelain lid, moistened with a few drops of *strong sulphuric acid*, stirred and heated to fumes, then cooled, will produce a blue color when breathed upon. The color disappears on heating, but reappears on cooling. Water destroys the color.

Molybdenite is very similar to graphite in appearance. It is distinguished from it by the fact that nitric reacts with molybdenite, $MoS_2$, leaving a white residue, but has no action upon graphite. The blowpipe gives $SO_2$ with molybdenite and $CO_2$ with graphite.

---

## SUGGESTION TO STUDENTS

Follow the procedure given on the following page determining molybdenum as lead molybdate. Avoid addition of a large excess of the lead salt in the precipitation of molybdenum and be sure that the excess is removed before ignition of the lead molybdate, otherwise some metallic lead will be formed with the precipitate.

After becoming familiar with the gravimetric method take up the study of the volumetric method for molybdenum.

### Preparation and Solution of the Sample

In dissolving the substance the following facts should be kept in mind. The metal is easily soluble in aqua regia; soluble in hot concentrated sulphuric acid, soluble in dilute nitric acid, oxidized by excess to $MoO_3$. It is dissolved by fusion with sodium carbonate and potassium nitrate mixture. It is insoluble in hydrochloric, hydrofluoric and dilute sulphuric acids.

The oxide $MoO_3$ is but slightly soluble in acids and alkalies; $MoO_2$ is insoluble in hydrochloric and hydrofluoric acids. $MoO_3$, as ordinarily precipitated, is soluble in inorganic acids and in alkalies. The oxide sublimed is difficultly soluble.

Molybdates of the heavy metals are insoluble in water, the alkali molybdates are soluble.

### General Procedures for Decomposition of the Sample and Separation from Interfering Substances

**Acid Method.** — About 0.25 to 5 grams of the sample (depending on the molybdenum content, about 0.15 g. desired) are treated in a flask with 15 cc. of $HNO_3$ and heated until the brown fumes are expelled. 5 to 10 cc. of HCl are added and the solution evaporated to dryness. The residue is taken up with about 100 cc. of hot water and the solution made strongly ammoniacal and heated to boiling and filtered hot. The residue of iron, etc. is washed several times with hot water. The filtrate is placed aside for subsequent use.

The precipitate, after puncturing the paper, is washed down into the flask in which the precipitation was made, using dilute HCl in sufficient amount to dissolve the hydroxides. Iron, alumina, etc. are again precipitated from a hot solution by adding ammonia, boiling, filtering and washing with hot water (at least five times). The filtrate is combined with the first. All the molybdenum is now in solution, and a separation from iron, aluminum, chromium, silicon is effected.

**Fusion Method.** — The sample is fused in an iron or nickel crucible with 8–10 parts of any of the following mixtures:

Sodium carbonate and peroxide (1 : 1)

Sodium hydroxide and peroxide (1 : 1)

Sodium or potassium carbonate with sodium nitrate (10 : 2)

Sodium peroxide.

The fusion is leached with hot water, boiled, filtered and washed. The residue is dissolved in $HNO_3$, the solution diluted to about 100 cc. and heated to near boiling and sodium hydroxide added in sufficient amount to completely precipitate iron, aluminum, etc. The precipitate is filtered off while still hot, and the filtrate combined with the water extract. All of the molybdenum is now in solution. The solution

is acidified with HCl and taken to dryness, to dehydrate the silica. Water is now added and the solution made ammoniacal and boiled, then filtered and the residue washed at least five times with hot water. Molybdenum passes into the filtrate.

**Molybdenum in Steel or Iron.** — The preparation of the sample does not differ materially from the general procedures already given. About 2 grams of the material are taken and dissolved in 25 cc.of HCl and 2 cc. of $HNO_3$, more $HNO_3$ (or $KClO_3$) being added to oxidize the iron if necessary. The solution is taken to dryness, taken up with water, boiled and poured into an excess of NaOH solution, preferably hot. Iron precipitates and molybdenum remains in solution. Resolution of the precipitate and reprecipitation is advisable, to prevent any loss due to occlusion of Mo in the precipitate. Molybdenum passes into the filtrate, the residue having been filtered and washed with hot water.

If the lead molybdate method is to be followed in presence of Ba, Sr, U, As, Cd, and Al, 10–15 cc. of HCl are added in excess of that necessary to neutralize the solution, and then sufficient ammonium acetate to combine with the free mineral acid. Ordinarily the procedure following makes allowance for the usual impurities present.

## GRAVIMETRIC METHOD FOR DETERMINING MOLYBDENUM

### PRECIPITATION AS LEAD MOLYBDATE

**Preliminary Remarks.** — This method is not interfered with by the presence of large amounts of acetic acid, lead acetate, or alkali salts (except sulphates). The paper need not be ignited separately and prolonged ignition at a much higher temperature than is necessary to destroy the paper does no harm. From faintly acid solution lead molybdate may be precipitated free from impurities in the presence of copper, cobalt, nickel, manganese, zinc, magnesium and mercury salts. It may be readily separated from iron and chromium. Barium, strontium, uranium, arsenic, cadmium and aluminum do not interfere if an excess of hydrochloric acid has been added to the solution followed by lead acetate and sufficient ammonium acetate to destroy the free mineral acid.

The method is not adapted to use with molybdenite, $MoS_2$, because of the suphate that forms on oxidation. Vanadium and tungsten must be removed.

**Special Reagents. Lead Acetate.** — A 4% solution is made by dissolving 20 grams of the salt in 500 cc. of warm water. A few cc. of acetic acid are added to clear the solution.

### PROCEDURE

The molybdenum in the form of soluble molybdate, as obtained under one of the procedures given under "decomposition of the sample" is diluted to a volume of approximately 350 cc. The solution is made acid with HCl, using methyl orange indicator, and about 5 cc. excess of HCl added. 5 to 10 grams of ammonium acetate and 2 to 5 cc. of acetic acid are now added. (The addition of a little ammonium nitrate is advantageous in preventing the formation of colloidal lead molybdate in the subsequent step.) The solution is placed on a hot plate and brought to boiling.

**Precipitation.** — To the hot solution is added slowly from a burette the lead acetate reagent, until a test drop taken from the solution gives no color change with a drop of freshly made tannic acid solution on a test plate. (Tannic acid 0.1 gram per 20 cc. of water). The disappearance of the brown color indicates that all the molybdenum has been removed from solution by precipitation. (1 cc. of the 4% lead acetate reagent will precipitate about 0.01 gram of molybdenum.) Now 2–5 cc. excess of the reagent are added and 5–10 cc. of acetic acid (amount depending on amount of Cu, Ca, Ni, Zn, Co, Mn, Cd, etc. present). The solution and precipitate is again placed on the hot plate, and boiled until the precipitate has crystallized and settled.

The precipitate is filtered hot. If the amount is large it is best to wash twice by decantation with 2 to 3% ammonium acetate and then on the filter five times. (The addition of ammonium acetate to the wash water assists in removal of the excess of lead.) The last three washings may be well accomplished with a 2 to 3% of ammonium nitrate.

**Ignition.** — The washed filter and precipitate are ignited at dull red heat in a porcelain crucible, until the precipitate becomes a yellowish white color. The residue is cooled in a desiccator and weighed as $PbMoO_4$.

$PbMoO_4 \times 0.2615 = Mo$. (See additional factors at end of text.)

*Notes.* — **Separation from Vanadium** is effected by a molybdenum sulphide precipitation in acid solution.

**Separation from Tungsten.** — Molybdenum, precipitated with tungsten by the lead molybdate method, is ignited and the mixture then treated with hydrochloric acid and a few drops of nitric acid and evaporated nearly to dryness. Dilute hydrochloric acid is added and the solution filtered. Tungsten remains undissolved.

Molybdenum may be precipitated by $H_2S$ as $MoS_2$ in presence of tartaric acid. Tungsten does not precipitate.

## VOLUMETRIC METHODS FOR THE DETERMINATION OF MOLYBDENUM OR MOLYBDIC ACID

### ESTIMATION BY REDUCTION WITH JONES REDUCTOR AND OXIDATION BY STANDARD PERMANGANATE SOLUTION

**Principle.** — The procedure depends upon the reduction of molybdic acid to $Mo_2O_3$ by passing its solution through a column of amalgamated zinc into a solution of ferric alum, and subsequent oxidation to $MoO_3$ by standard potassium permanganate solution.

**Reactions.** — $2MoO_3 + 3Zn = Mo_2O_3 + 3ZnO.$

$$5Mo_2O_3 + 6KMnO_4 + 9H_2SO_4 = 10MoO_3 + 3K_2SO_4 + 6MnSO_4 + 9H_2O.$$

The reductor shown in Fig. 89 should contain a column of 20 mesh amalgamated zinc $\frac{3}{4}$ inch in diameter and 10 inches long. If the molybdenum solution is given a preliminary reduction by heating with 2 grams of 20 mesh zinc for the purpose of precipitating copper (which is subsequently removed by filtration on asbestos), the length of the zinc column may safely and advantageously be reduced to 8″. The lengths specified apply only to a column $\frac{3}{4}$ inch in diameter; the lengths for tubes of different diameters would have to be determined experimentally. The zinc should be as free from iron and as low in other impurities as possible.

If the reductor has been standing idle for longer than one day it is cleaned by passage of 50 cc. of 6 % sulphuric acid, and 50 cc. of water, both at room temperature, a small amount of the water being left in the funnel which forms the reductor inlet. The acid and water are discarded after having been passed through the reductor. These operations are only necessary when the reductor has been standing idle for some time.

The required amount of ferric phosphate solution and sufficient water (about 50 cc.) to cause the tip of the reductor outlet tube to dip beneath the surface of the liquid are added to the flask.

The molybdenum solution (volume 50 to 100 cc., acidity 6 % $H_2SO_4$) which may be at room temperature or slightly warm, is passed through the reductor rapidly. The total time required for the passage of the molybdenum solution and the liquids which follow it need not exceed from 1 to 3 minutes. No advantage results from having the solution hot — on the contrary, the greater action of the hot acid solution on the zinc is a disadvantage. No increase in accuracy is obtained by passing the solution through the reductor at a slower rate than that specified.

Fig. 89. — Reductor Tube.

When the funnel which forms the inlet of the reductor is nearly but not entirely empty, 150 cc. of water at room temperature are passed through the reductor. In the case of samples containing relatively small amounts of molybdenum, 100 cc. of water is sufficient. In no case is the funnel permitted to become entirely empty and the stopcock is closed while some of the wash water remains above the surface of the zinc.

The solution is titrated with N/10 $KMnO_4$ solution.

One cc. of N/10 $KMnO_4 = \frac{.0144}{3}$ gram of $MoO_3 = \frac{.0096}{3}$ gram of molybdenum.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Determination of Molybdenum in Wulfenite or Molybdenite [1]

**Procedure.** — 1. Solution. One gram of the finely ground ore is dissolved by treatment with 15 cc. of nitric acid (sp.gr. 1.42) and 7 cc. of sulphuric acid (sp.gr. 1.84) at a temperature just short of boiling in a 150 cc. covered beaker. When practically complete decomposition has been effected, the liquid is evaporated until fumes of sulphur trioxide are freely expelled. After cooling addition is made of about 40 cc. of water, the solution is boiled to dissolve the molybdenum, cooled to room temperature and filtered into a 250 cc. beaker. The residue, consisting of lead sulphate, silica, etc., is washed with very dilute $H_2SO_4$.

The residue rarely, if ever, contains Mo, nevertheless it should be examined to make sure that decomposition is complete. To this end it is digested with 15 cc. to 25 cc. of ammonium acetate solution (prepared by mixing 8 cc. of $NH_4OH$(0.90) with 10 cc. of $H_2O$ and adding 7 cc. of 99 % $C_2H_4O_2$) to remove all lead sulphate. The filter paper is washed with hot dilute acetic acid and with water. It is then ignited in a platinum crucible and the silica is removed by treatment with a drop of sulphuric acid and several cc. of hydrofluoric acid and evaporating to the expulsion of sulphuric acid. If an appreciable residue remains after this treatment, it is fused with potassium pyrosulphate and tested for molybdenum by means of tartaric acid and ammonium sulphide as described later.

2. To the solution containing all of the molybdenum there is added sufficient ferric sulphate to provide ten times as much iron as there is arsenic present, (the ratios of iron to the salts are as follows: —

$$(Fe \rightarrow FeSO_4(NH_4)_2SO_4.6H_2O\ 1:7 \text{ or } Fe \rightarrow Fe_2(SO_4)_3.9H_2O\ 1:10)$$

from 0.2 to 0.3 gram of iron is usually ample. The acid solution is then nearly neutralized with ammonia (addition of a sufficient amount to impart a red tint to the clear yellow solution *is to be avoided*), heated nearly to boiling and poured very slowly and with vigorous stirring into 75 cc. of warm ammonia solution (15 cc. = $NH_4OH$ 1.90 sp.gr. 60 cc. of $H_2O$) contained in a 250 cc. beaker. When it has settled the ferric hydroxide (which will carry down quantitatively all arsenic in the ore) is filtered and washed thoroughly with hot water. The filtrate containing the molybdenum is set aside for subsequent treatment.

The $Fe(OH)_3$ precipitate is dissolved in a slight excess of hot dilute (1 : 4) sulphuric acid and the resulting solution is again heated to boiling and poured into 75 cc. of warm ammonia solution as before;

[1] Method of Ledoux and Co. and the Electro Metallurgical Co., by A. M. Smoot and J. A. Holladay.

the iron hydrate is again washed. The two filtrates, which will contain all the molybdenum, are united in a 600 cc. beaker.

It is essential that arsenic, which is usually present in these ores, be eliminated, and the method described furnishes a simple and effective way for accomplishing this. The addition of ferric sulphate would be omitted only in case arsenic is known to be absent or when the ore itself carries sufficient iron to take care of the arsenic.

3. To the combined ammoniacal filtrates there are added 2 grams of tartaric acid and when the acid has dissolved the liquid is saturated with hydrogen sulphide. The presence of tartaric acid is necessary to prevent precipitation of vanadium and tungsten along with the molybdenum.

Both of these elements are ordinary constituents of wulfenite concentrates. Under these conditions the molybdenum remains in the solution as ammonium thiomolybdate, $(NH_4)_2MoS_4$, which imparts a deep red color to the solution. If a small precipitate of insoluble sulphides separates out, it is filtered off and washed with dilute ammonium sulphide solution; if the solution remains clear this step is omitted. Copper in the amounts usually present remains entirely in solution at this point and is reprecipitated with molybdenum when the solution is subsequently acidified.

4. The thiomolybdate solution is made slightly acid with sulphuric acid (1 : 2), molybdenum precipitates as trisulphide.

The cessation of effervescence on addition of more acid and the disappearance of the red color of the ammonium thiomolybdate mark the point where sufficient acid has been added to complete the reactions.

5. After heating for a short time, the precipitate is allowed to settle and filtered on an 11 cm. paper and washed thoroughly with hydrogen sulphide water containing a small amount of sulphuric acid. Addition of paper pulp aids the filtration.

5a. Note. The filtrate from the molybdenum sulphide sometimes contains appreciable amounts of molybdenum; addition is made to it of 15 cc. of nitric acid (sp.gr. 1.42) and the solution is evaporated to fumes of sulphur trioxide, more sulphuric acid being added if sufficient is not already present. After allowing it to cool, 5 cc. of concentrated nitric acid are added and the solution is again evaporated to fumes. The addition of nitric acid and evaporation to strong fumes is repeated once more to insure the destruction of all organic compounds. After allowing to cool, sufficient water is added to dissolve all salts, two grams of tartaric acid are added, and after addition of an excess of ammonia (sp.gr. 0.90) the warm liquid is thoroughly saturated with washed hydrogen sulphide and filtered. The filtrate is acidified with sulphuric acid (1:2) and if after standing for fifteen to thirty minutes in a warm place any molybdenum trisulphide has separated out it is filtered, washed well with hydrogen sulphide water containing a small amount of sulphuric acid, and combined with the main precipitate. The precipitation of the molybdenum as sulphide when carried out as described effects the separation and removal of tungsten, vanadium and chromium.

6. The molybdenum sulphide precipitate and paper, or precipitates and papers, are put into a 250 cc. beaker and treated with 6 cc. of sulphuric acid (sp.gr. 1.84) and 10 cc. of nitric acid (sp.gr. 1.42) and

the liquid is cautiously boiled until dense fumes of sulphur trioxide are freely evolved. After allowing it to cool somewhat, 5 cc. of nitric (sp.gr. 1.42) are added and the evaporation is repeated. The evaporation with 5 cc. portions of strong nitric acid is repeated several times until the filter paper has been completely destroyed and every trace of yellow color, due to carbonaceous matter, has disappeared. When this has been accomplished the solution is fumed strongly for a short while, cooled, 5 cc. of water added and the liquid again taken to fumes of sulphur trioxide in order to insure the expulsion of every trace of nitric acid.

7. When cool, addition is made of approximately 75 cc. of water and the contents of the beaker are boiled for a few minutes, which should give a perfectly clear solution. Five grams of granulated zinc (0.002% iron or under) are then added and the solution is warmed until most of the zinc has dissolved; this results in partial reduction of molybdenum and complete precipitation of copper, which is usually present.

8. The liquid is then filtered on an asbestos or "alundum" filter to remove the undissolved zinc and the copper.

9. All the molybdenum in the solution is then reduced from the sexivalent to the trivalent condition by passage through the zinc reductor into a solution of ferric sulphate containing phosphoric acid.

10. The solution is then titrated with N/10 permanganate.

The details of the reductor and the method of preparing it are given on page 393.

It is essential to run a blank determination, using the same quantity of zinc that was used to separate copper and the same volumes of water and acid — passing the solution through the reductor under the same conditions. With good zinc the correction may be about 0.2 cc.

$$1 \text{ cc. N/10 } KMnO_4 = \frac{.0144}{3} \text{ gram of } MoO_3 \text{ and} = \frac{.0096}{3} \text{ gram of Mo.}$$

1 cc. of N/10 $KMnO_4$ = .0048 g. $MoO_3$ and .0032 g. of Mo.

Fe factor of $KMnO_4 \times 0.5725$ = Mo factor.

## METHOD FOR DETERMINING MOLYBDENUM AND VANADIUM WHEN PRESENT IN THE SAME SOLUTION

**Principle of the Method.** — The procedure depends upon the fact that vanadic acid alone is reduced by $SO_2$ in a sulphuric acid solution, whereas both vanadic and molybdic acids are reduced by amalgamated zinc, in each case the reducing agents forming definite lower oxides which are readily oxidized to definite higher oxides by $KMnO_4$.

**Reactions.**

$SO_2$ Reduction:

1. $V_2O_5 + SO_2 = V_2O_4 + SO_3$. (No action on $MoO_3$.)

Zn Reduction:

2. $V_2O_5 + 3Zn = V_2O_2 + 3ZnO$.
3. $2MoO_3 + 3Zn = Mo_2O_3 + 3ZnO$.

$KMnO_4$ Oxidation:

4. $5V_2O_4 + 2KMnO_4 + 3H_2SO_4 = 5V_2O_5 + K_2SO_4 + 2MnSO_4 + 3H_2O$.
5. $5V_2O_2 + 6KMnO_4 + 9H_2SO_4 = 5V_2O_5 + 3K_2SO_4 + 6MnSO_4 + 9H_2O$.
6. $5Mo_2O_3 + 6KMnO_4 + 9H_2SO_4 = 10MoO_3 + 3K_2SO_4 + 6MnSO_4 + 9H_2O$.

From the reactions "4" and "5" it is seen that three times the amount of $KMnO_4$ is required to oxidize $V_2O_2$ to $V_2O_5$ as is required in the case of $V_2O_4$, hence — total cc. $KMnO_4$ required in oxidation of the zinc-reduced oxides minus three times the cc. $KMnO_4$ required in oxidizing the tetroxide of vanadium formed by the sulphur dioxide reduction = cc. $KMnO_4$ required to oxidize $Mo_2O_3$ to $MoO_3$. From these data molybdenum and vanadium may readily be calculated.

**Method of Procedure.** — *A.* **Vanadic Acid.** — The solution containing the vanadic and molybdic acids in a 250 to 300 cc. Erlenmeyer flask, is diluted to 75 cc., acidified with 2 to 3 cc. of strong sulphuric acid, heated to boiling and the vanadic acid reduced by a current of $SO_2$ passed into the solution until the clear blue color indicates the complete reduction of the vanadic acid to $V_2O_4$. The boiling is now continued and $CO_2$ passed into the flask to expel the last trace of $SO_2$.

Standard N/10 $KMnO_4$ is now run into the reduced solution to the characteristic faint pink. From reaction "4," vanadic acid may be calculated.

One cc. of N/10 $KMnO_4$ = .0182 gram $V_2O_5$ = .0051 gram vanadium.

*B.* **Molybdic Acid.** — The reduction by Jones' reductor, and titration of the combined acids reduced by amalgamated zinc with N/10 potassium permanganate solution, is carried out exactly as described in the determination of molybdic acid alone. In this case 50 cc. of 10% ferric alum and 8 cc. of the phosphoric acid is placed in the receiving flask.

**Calculation.** — Total permanganate titration in *B* minus three times the titration in *A* gives the permanganate required to oxidize $Mo_2O_3$ to $MoO_3$. From equation 6 the molybdic acid may now be calculated.[1]

One cc. of N/10 $KMnO_4$ = 0.0048 gram of $MoO_3$ = 0.0032 gram of molybdenum.

[1] The Editor acknowledges valuable assistance received from Messrs. A. M. Smoot, Technical Director, Ledoux & Co., and J. A. Holladay, Chemist Electrometallurgical Co., and J. P. Bonardi, Mines and Smelter Supply Co.

## NICKEL

**Ni, at. wt. 58.68; sp.gr. 8.6–8.9; m.p. 1452° C.; oxides, NiO, $Ni_2O_3$, $Ni_3O_4$.**

The determination of nickel is required, principally, in the analysis of ores, metallic nickel and its alloys, but is also required in the analysis of metallic cobalt and cobalt products as well as in a host of miscellaneous materials.

In the majority of cases the results of a nickel determination are calculated in terms of metallic nickel. Even in the determination of nickel in nickel-plating solution the results are calculated in terms of metallic nickel since this is the factor by which the solutions are controlled.

### OCCURRENCE

Nickel occurs native only in meteoric iron. It is found combined in a number of minerals.

**Minerals.** — *Millerite*, Capillary Pyrites, NiS, a brass-colored, opaque mineral with metallic lustre, occurring in hair-like or in needle crystals, often interwoven in crusts; greenish-black streak; hardness 3–3.5.

*Niccolite*, Copper Nickel, NiAs, a massive, pale copper-red, opaque, brittle mineral with metallic lustre, fine-grained structure; streak brownish-black; hardness 5–5.5.

*Garnierite*, Noumeit, $H_2(Ni.Mg)SiO_4 \times H_2O$, a pale greenish-white to dark green, brittle, opaque, mineral with vitreous to dull lustre, loosely packed earthy mass; streak light green to white; hardness 2–3.

Pentlandite, (Fe,Ni)S; Annabergite, $Ni_3(AsO_4)_2.8H_2O$, Chloanthite, $NiAs_2$.

### DETECTION

After bringing the sample into solution by one of the methods described under Preparation and Solution of the Sample, silica is removed, if present, in the usual manner, by evaporating the solution to dryness in the presence of an excess of hydrochloric acid, dissolving the residue and boiling with hydrochloric acid and filtering off the silica.

**Dimethylglyoxime** will precipitate nickel as oxime from an acetic acid solution containing sodium acetate and in this manner separate it from cobalt, manganese and zinc. After precipitating iron, aluminum and chromium and filtering them off, the solution is slightly

acidified with hydrochloric acid, then is neutralized with sodium hydroxide, and acidified with acetic acid. A solution of dimethylglyoxime is added, when nickel, if present, will be precipitated as a flocculent red precipitate.

Nickel may be detected in the presence of cobalt by adding a solution of sodium hydroxide to the solution of cobalt and nickel until a slight precipitate is formed, then somewhat more potassium cyanide than is necessary to redissolve the precipitate and finally two volumes of bromine water. Warm gently and allow to stand for some time. If a precipitate of nickel hydroxide separates, filter, wash and test with the borax bead.

**Alpha benzildioxime** added to an ammoniacal solution of nickel precipitates an intensely red salt having the composition $C_{28}H_{22}N_4O_4Ni$. This precipitate is very voluminous. Silver, magnesium, chromium, manganese and zinc do not interfere with this reaction.

## METHODS FOR THE DETERMINATION OF NICKEL

### Preparation and Solution of the Sample

Nickel, chemically, is not an active element. It is not attacked at ordinary temperatures by air or by water. Organic acid attacks it but feebly after long periods of contact. Sulphuric and hydrochloric acid dissolve it slowly. It is readily attacked, however, by nitric acid. Alkalies in molten condition or in water solution have little effect on the element.[1]

The materials in which nickel occurs ordinarily, may, in general, be brought into solution by treatment with acids, but in the case of some refractory ores and alloys, a fusion is required first to make the acid treatment effective. When treating ores containing sulphides or arsenides a strong oxidizing treatment is necessary to break up these compounds. Metallic nickel, as stated above, is best dissolved by treating with nitric acid. Nickel alloys may be dissolved in a mixture of hydrochloric acid and nitric acid.

**General Procedure for Ores.** — One gram of the finely powdered ore is weighed into a porcelain dish and mixed intimately with 3 grams of powdered potassium chlorate. The dish is covered with a watch-glass and 40 cc. of concentrated nitric acid added slowly. The dish is allowed to stand in a cool place for a few minutes, then placed on a water bath and digested until the sample is completely decomposed, stirring the mixture frequently with a glass stirring rod, and adding a little potassium chlorate from time to time until the decomposition is complete. The watch-glass is then removed and any particles that may have spattered on it are washed back into the dish and the evaporation continued to dryness. This evaporation to dryness is repeated with the addition of 10 cc. of concentrated hydrochloric acid, and the silica dehydrated by heating for an hour or more in an air oven at 110° C. The dry residue is moistened with concentrated hydrochloric acid and the sides of the dish washed down with hot water, the mixture heated to boiling and allowed to boil for a few minutes, then withdrawn from the heat and filtered, hot, after the insoluble matter has settled.

Treat the filtrate for the removal of interfering elements as directed under Separations.

**Fusion Method.** — The above method is used where it is desired to determine insoluble matter or "gangue." As a method of bringing the nickel in the sample into solution it is quite satisfactory and when the insoluble matter burns to a pure white ash the ignited residue may be weighed as silica, but in some cases this method does not give sufficient information regarding the composition of the gangue.

If it is necessary to make a complete analysis it is usually better

[1] Footnote Ref. Cir. 100 U. S. Bureau of Standards.

to fuse the sample with the sodium and potassium carbonate mixture containing a little potassium nitrate and then treat in the usual manner to determine silica.

**Potassium Bisulphate Fusion.** — In the treatment of nickel and cobalt oxides these are ground to a fine powder and a representative sample of 1 gram is fused with 10 grams of potassium bisulphate. This may be done in a porcelain or silica crucible or dish or in a "Low" decomposition flask. See Introduction § 24, 3. The melt is extracted with water and the silica filtered off.

**Solution of Metallic Nickel and Its Alloys.** — From 1 to 5 grams of the well-mixed drillings are treated with a minimum quantity of nitric acid and 20 cc. 1 : 1 of sulphuric acid added and the solution evaporated to fumes of sulphur trioxide. The fuming is continued for ten minutes. The concentrate is diluted carefully with a little water and the insoluble filtered off.

## GRAVIMETRIC DETERMINATION OF NICKEL

### PRECIPITATION OF NICKEL BY DIMETHYLGLYOXIME

This method has been demonstrated by O. Brunck (Zeit.f.ang. Chem., 20, 1844) to be the most accurate and expeditious procedure known for nickel. By this method one part of nickel may be detected in 400,000 parts of water in presence of 5,000 parts of cobalt. The nickel precipitate with this reagent is almost completely insoluble in water and is only very slightly soluble in acetic acid, but is easily decomposed by strongly dissociated acids, so that the precipitate is incomplete in neutral solutions of nickel chloride, nitrate, or sulphate, owing to the formation of free acid by the reaction.

**Reaction:** $2(CH_3)_2C_2N_2O_2H_2 + NiCl_2 = [(CH_3)_2C_2N_2O_2H]_2.\ Ni + 2HCl.$

The free acid that is formed is neutralized with sodium, potassium or ammonium hydroxides, or by addition of the acetate salts of these bases, and nickel is completely precipitated from the solution, not even a trace being found in the filtrate.

The quantitative determination of nickel in the presence of other metals is a simple operation. The nickel should be in the form of a convenient salt.

The concentration of the solution does not matter, the precipitation can take place in a solution highly concentrated, or in very dilute solution. The reaction is not hindered by the presence of ammonium salts.

Iron, alumina, chromium, cobalt, manganese and zinc do not interfere. Copper may be present to an extent of sixty per cent of the material examined. With higher per cents of copper, it is advisable to redissolve the precipitate with dilute hydrochloric acid and after addition of 5–10 cc. of the reagent (dimethylglyoxime) reprecipitate the nickel by making the solution ammoniacal. An excess of ammonia is necessary to prevent the copper, if present in large amount, from precipitating with the nickel. A large excess of ammonia is to be avoided, however, as the oxime is soluble in ammonia.

Theoretically, four parts of dimethylglyoxime (as a salt i.e. 40 cc. of the reagent to 0.1 g. of Ni) added as a 1% alcoholic solution, are necessary for one part of nickel, but an excess is usually required, and a large excess does no harm, provided the volume of the alcohol does not exceed more than a half of the water solution containing the nickel, as alcohol has a solvent action on the nickel oxime.

The compound is very stable and volatilizes, undecomposed at 250° C. If confined, however, it may be ignited to the oxide NiO. This may be accomplished by enclosing the compound in a wet filter, carefully folded, the filter charred, without burning, and the

heat gradually raised to redness, the crucible being covered. The ignition is completed with uncovered crucible.

**Reagents. — Dimethylglyoxime,** $(CH_3)_2C_2(NOH)_2$. Ten grams of the salt are dissolved in 1000 cc. of strong alcohol. Theoretically 40 cc. of the reagent are required to precipitate 0.1 gram of nickel. In practice 50 cc. are used; a larger amount does no harm.

**Tartaric or Citric Acid.** — 50% solution. Use 15 cc. per gram of iron in the sample.

**Method of Procedure.** — 1. Solution of the Sample — Under "Preparation and Solution of the Sample" select the method for the special class of material being examined and treat according to the directions given. The quantity of the sample taken for the precipitation is governed by the amount of nickel present. This nickel content should not exceed 0.1 gram of Ni, as the nickel glyoxime is voluminous and difficult to handle in large amounts. If a large sample is taken it may be dissolved, made to a definite volume and an aliquot portion taken for precipitation.

2. If hydrogen sulphide has been used, expel this by boiling the acid solution and dilute the solution to about 300 cc.

3. Add ammonium hydroxide in just sufficient quantity to neutralize the free acid and then a few drops in excess. Observe whether a precipitate forms. If it does, add more ammonia and observe whether this redissolves. (If $H_2S$ treatment has been omitted copper if present will appear here, but redissolves in an excess of ammonia.) Iron, chromium, aluminum will precipitate if present.

4. If a precipitate forms, add tartaric or citric acid solution, (which prevents precipitation of iron, aluminum and chromium) 5 cc. if these impurities are present in comparatively small amounts or 15 cc. in analysis of steel alloys. Add also 5–10 cc. of ammonium chloride (10% solution) to keep any zinc, manganese or magnesium in solution.

5. Again make ammoniacal with ammonia. If a precipitate forms, which persists with additional ammonia, dissolve by addition of hydrochloric acid and then make ammoniacal. This generally is sufficient to give a clear solution. (The tartaric or citric acid reagents should be filtered if cloudy, before using.) If not, add more tartaric or citric acid and repeat the operation.

6. To the clear solution add 50 cc. of the dimethylglyoxime reagent per 0.1 gram of nickel present, or five times by weight (in terms of the salt) of the nickel present.

7. Add ammonium hydroxide to neutralize the acid formed by the reaction, and then a sufficient excess so that the solution is distinctly ammoniacal, but not a large excess. The precipitation of the scarlet-red nickel glyoxime, is hastened by stirring. Place the mixture on a warm plate for about 30 minutes to an hour. Do not boil, and avoid a free flame as the alcohol is inflammable. Test the clear solution

for nickel with more of the reagent, to be sure that a sufficient amount has been added.

8. Filter into a weighed Gooch crucible. (A platinum Gooch with platinum mat is excellent for this purpose.) A filter paper with a counterbalance filter paper, may be used in place of the Gooch, the counterbalanced paper being treated with the reagents just as if it contained the precipitate. It is dried alongside of the other paper and again used as a counterbalance when the salt is weighed.

9. Wash the compound free of impurities. Ten washings should be sufficient. (If the compound is dark reddish-brown, dissolve in dil. HCl and reprecipitate by adding $NH_4OH$ and about 10 cc. of the glyoxime reagent.)

10. Dry the precipitate at 110°–120° C. for about 1 hour, and weigh. Repeat the drying in the oven for another 10 minutes and again weigh. If the weight has remained constant, calculate the nickel present. The salt should be dried to constant weight.

11. The glyoxime contains 20.32% nickel. Hence the weight multiplied by 0.2032 gives the nickel in the compound. Calculate the per cent in the sample analyzed.

NOTE. The sample should not contain over 0.1 gram of cobalt. If much cobalt is present use about 7 : 1 of the reagent in place of 5 : 1. The cobalt oxime is soluble in the reagent.

## PRECIPITATION OF NICKEL BY ELECTROLYSIS

This precipitation is conducted in exactly the same manner as the one described under Cobalt for the Precipitation of Cobalt by Electrolysis, and requires that the same precautions be exercised in the practice of the method.

In the presence of cobalt the two elements may be determined together by electrolysis as described below and the deposited metal redissolved and the two elements separated by one of the methods given under Cobalt or Nickel.

**Procedure.** — After the sample has been brought into solution by one of the methods outlined under Preparation and Solution of the Sample, the solution is evaporated with 20 cc. of 1 : 1 sulphuric acid for every gram of metal in the sample. The evaporation is continued until the solution has fumed strongly for ten minutes. Cool carefully and dilute with 20 cc. of water. Heat the solution to nearly boiling and pass hydrogen sulphide for one hour to precipitate members of the second group. This long treatment is necessary to insure complete precipitation of arsenic.[1] Filter and boil to expel hydrogen sulphide. Add 5 cc. of nitric acid to insure oxidation of iron compounds to the ferric state and add ammonium hydroxide until just slightly

[1] The addition of a small piece of filter paper to the material during the fuming stage will reduce the arsenic and hasten its precipitation as sulphide, shortening the time stated above.

alkaline. Filter off the ferric hydroxide and wash with water containing a small quantity of ammonium hydroxide. To recover occluded nickel dissolve the precipitate in hydrochloric acid and reprecipitate the iron with addition of a little hydrogen peroxide. Combine the filtrates. Evaporate to about 250 cc. and add 50 cc. of strong ammonium hydroxide and electrolyze as described under Cobalt, page 234.

The increase in weight of the electrode is the weight of cobalt and nickel in the sample. The percentage of cobalt and nickel in the sample is found by multiplying the increase in weight of the electrode by 100 and dividing by the weight of the sample.

NOTE. The deposition of cobalt and nickel by the above method has been found to be the most accurate of the electrolytic methods. In the solutions containing the organic acids there is always more or less carbide deposited on the cathode with the metal. This causes high results.

## VOLUMETRIC METHOD FOR NICKEL

### POTASSIUM CYANIDE METHOD FOR NICKEL

The method is rapid and accurate and is especially adapted for determining nickel in steel. Iron, manganese, chromium, zinc, vanadium, molybdenum and tungsten do not interfere. Copper, however, should be removed if present. The method depends upon the selective action of potassium cyanide for nickel in preference to silver iodide, used as an indicator, the reactions taking place as indicated, the solution being slightly alkaline with ammonia:

(*a*) $Ni(NH_3)_6SO_4 + 4KCN = K_2Ni(CN)_4 + K_2SO_4 + 6NH_3$ (N.B. $4KCN \simeq Ni$)

(*b*) $AgI + 2KCN = KAg(CN)_2 + KI$ (N.B. $2KCN \simeq Ag$)

**Reagents.** — *N/10 Silver Nitrate.* 10.788 grams of pure silver are dissolved in nitric acid and made to 1000 cc. or 16.99 g. of the silver nitrate salt. (See Index for reagent.) 1 cc. $\simeq$ 0.01302 g. of KCN.

If preferred the reagent may be made to be equivalent to about 0.001 gram of Ni per cc. by dissolving 5.85 grams of $AgNO_3$ per liter.

*Potassium Iodide.* — 25% solution.

*N/10 Potassium Cyanide.* — 13.5 grams of pure KCN are dissolved in water, 5 grams of KOH added and the solution made to 1000 cc.

The cyanide solution is standardized against the silver nitrate solution.

If it is desired to have a solution equivalent to 0.001 g. of Ni, 5 grams of KCN per liter is the approximate strength required.

**Standardization of the Cyanide.** — Fifty cc. of the KCN solution are diluted to about 150 cc., 5 cc. of the KI reagent added and the solution titrated with the standard $AgNO_3$ reagent until a faint permanent opalescence is obtained. A drop of the KCN solution should be sufficient to clear this. Note the number of cc. required and calculate the normality factor of the cyanide in terms of the silver nitrate reagent.

*Example.* — Suppose 49 cc. of the silver nitrate reagent were required for the 50 cc. of the cyanide solution, then the normality would be $49 \div 50 \times N/10$ or 0.98 N/10.

1 cc. N/10 solution is equivalent to 0.002934 gram of nickel.

The reagent may be standardized against a nickel steel of the U.S. Bureau of Standards, following the procedure given below and calculating as follows:

$$\text{Nickel factor} = \frac{\text{Gram Ni in standard taken}}{(\text{cc. KCN required}) - (\text{cc. KCN equivalent to 5 cc. } AgNO_3)}$$

**Citric Solution.** — 200 grams of $(NH_4)_2SO_4$, 150 cc. of concentrated $NH_4OH$ and 120 grams of citric acid per 1000 cc.

**Procedure.** — One gram of the steel drillings or such an amount of material as contains not over 0.1 g. of Ni, is dissolved in a beaker with 20 cc. of hydrochloric acid (1 : 1). When action ceases 10 cc. of nitric acid (1 : 1) are added and the solution boiled until the red nitrous acid fumes are driven off.

About 100 cc. of the citrate solution are added. If 2 per cent or more of chromium is present the amount of citrate solution is doubled. The solution is now diluted to about 250 cc.

Exactly 5 cc. of the standard silver nitrate solution are now added from a pipette or burette, and then ammonium hydroxide, drop by drop, until the cloudiness caused by the silver chloride just disappears. Two cc. of the potassium iodide solution are now added.

The solution is titrated with the standard potassium cyanide solution with constant stirring until the turbidity just disappears. The end-point is reached when there is no longer a distinction in clearness of the drop of the reagent and its surrounding liquid to which it is added.

If the end point is passed, a measured amount of silver nitrate (5–10 cc.) is added and the cyanide titration repeated.

**Calculation.** — Deduct the cc. KCN equivalent of the total silver nitrate solution used from the total cc. of the KCN solution required in the titration. The remainder is the potassium cyanide required by the nickel.

The cc. of KCN required by Ni multiplied by the factor for Ni = gram of nickel in the sample.

### Notes

1. A large excess of ammonia is to be avoided as the AgI is soluble in a large excess.

2. The presence of sulphates increases the sensibility of the end-point.

3. The silver nitrate solution should not be stronger than that indicated in the method as there is danger of the iodide of silver settling out as a curdy precipitate in stronger solutions.

4. A white film is apt to form on the surface of the liquid if exposed to the air for some time. This produces no error.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Volumetric Determination of Nickel in Alloys

This method, as described by S. W. Parr and J. M. Lindgren,[1] consists of a modification of the dimethylglyoxime method. The precipitation takes place in the usual manner and the precipitate is dissolved in sulphuric acid and the excess titrated with a standard solution of potassium hydroxide.

**Procedure.** — The alloy is dissolved in nitric or hydrochloric acids and if iron, aluminum or chromium are present twice their weight of tartaric acid is added to prevent their precipitation. If chromium is present ammonium chloride is also added. If manganese or zinc is present hydrochloric acid should be used and most of the free acid evaporated. Add a few cc. of hydrogen peroxide to oxidize any ferrous iron to the ferric state. Dilute to 300 or 400 cc. and neutralize the free acid by sodium acetate. Heat the solution to nearly boiling and add five times as much dimethylglyoxime, in 1% alcoholic solution, as the nickel present. Then completely neutralize with ammonium hydroxide, using a very slight excess (or the solution may be neutralized with sodium acetate). Heat until all the nickel is precipitated. Filter and wash. Place the precipitate and filter in a beaker, add an excess of 0.05N sulphuric acid, dilute to 200 cc., heat until solution is complete and titrate back with 0.1N potassium hydroxide solution, taking the first faint yellowish tinge as the end-point. The solutions are standardized against pure nickel.

NOTE. Cobalt should not exceed 0.1 gram per 100 cc. and an excess should be used of the dimethylglyoxime.

### Nickel in Nickel-plating Solutions

In most cases it is quite unnecessary to separate the cobalt from the nickel in making this determination and, as the principal impurity is usually iron, the best practice is to follow the method given under Precipitation of Cobalt by Electrolysis, page 234.

If chlorides or organic matter are present in the solution the preparation of the solution for electrolysis is accomplished in the following manner:

From the well-stirred solution in the plating tank, withdraw about 200 cc. and place in a small beaker. Prepare a 100 cc. burette by thoroughly cleaning it with the sulphuric acid and potassium bichromate mixture and distilled water. Wash finally with a few cc. of the nickel solution and fill the burette with the solution from the plating tank.

[1] S. W. Parr and J. M. Lindgren, Trans. Am. Brass Founders' Assoc., 5, 120–9.

Run 66.7 cc. into an evaporating dish and add 2 cc. of 1 : 1 sulphuric acid. Evaporate to fumes of sulphur trioxide and allow to fume strongly for ten minutes. Dissolve in a little water. Dilute to 200 cc. carefully, neutralize with a solution of ammonium hydroxide and add 50 cc. of strong ammonium hydroxide and electrolyze. (See Precipitation of Cobalt by Electrolysis.)

The increase in weight of the cathode in grams multiplied by 2 gives the weight in ounces of nickel in one United States gallon of the plating solution.

The author is indebted to Dr. W. L. Savell for a considerable portion of the material appearing in this chapter.

## NITROGEN

**Element, $N_2$, at.wt. 14.01; D. (air) 0.9674; m.p. −210°; b.p. −195.5° C.; oxides, $N_2O$, $N_2O_2$, $N_2O_3$, $N_2O_4$, $N_2O_5$.**

**Ammonia. $NH_3$, m.w. 17.03; D. (air) 0.5971; sp.gr. liquid 0.6234; m.p. −77.3°; b.p. −38.5° C. Crit. temp. 130°; liquid at 0° with 4.2 atmospheres pressure. Commercial 28% $NH_3$, sp.gr. 0.90.**

**Nitric Acid. $HNO_3$, m.w., 63.02; sp.gr. 1.53; m.p. −41.3; b.p. 86° C. Boiling-point of commercial 95% acid is a little above 86°, but gradually rises to 126° and the strength of acid falls to 68.9%, sp.gr. is then 1.42. The acid now remains constant, the distillate being of the same strength.**

### OCCURRENCE

**Element.** — Free in air to extent of 78% + by volume and 76% − by weight.

**Air** weight of 1 liter = 1.293 grams. With oxygen as 32, air = 28.95

Composition of Air. On the Basis of 1000 Liters of Atmosphere

| Element | Liters per 1000 l. | Weight per 1000 l. grams | Per cent by Vol. | Per cent by Wt. |
|---|---|---|---|---|
| Nitrogen | 780.3 | 975.80 | 78.1 | 75.47 − |
| Oxygen | 209.9 | 299.84 | 21.0 | 23.19 − |
| Argon | 9.4 | 16.76 | 0.9 | 1.296 + |
| Carbon dioxide | 0.3 | 0.59 | 0.04 | 0.045 |
| Hydrogen | 0.1 | 0.01 | | |
| Neon | 0.015 | 0.01339 | | |
| Helium | 0.0015 | 0.00027 | | |
| Krypton | 0.00005 | 0.00018 | | |
| Xenon | 0.000006 | 0.00003 | | |

1000 liters of water-saturated air contains 4.9 grams at 0°, 17.2 grams at 20° and 55 grams of $H_2O$ at 40° C. Ordinarily 50 to 70% of this is present.

Nitrogen is found combined in nature as potassium nitrate (saltpeter), $KNO_3$; sodium nitrate (Chili saltpeter), $NaNO_3$, and to a less extent as calcium nitrate, $Ca(NO_3)_2$. It occurs in plants and in animals, in the substances proteids, blood, muscle, nerve substance, in fossil plants (coal), in guano, ammonia and ammonium salts.

**Free nitrogen** is estimated in the complete analysis of gas mixtures. In illuminating gas the other constituents are removed by combustion and absorption and the residual gas measured as nitrogen.

**Total nitrogen** in organic substances is best determined by decomposition of the materials with sulphuric acid as described later, and estimating the nitrogen from the ammonia formed.

**Combined nitrogen** in the form of ammonia and nitric acid specially concerns the analyst. In the evaluation of fertilizers, feedstuffs, hay, fodders, grain, etc., the nitrogen is estimated after conversion to ammonia. Ammonia, nitrates and nitrites may be required in an analysis of sewages, water, and soils. Nitric acid is determined in Chili saltpeter, in the evaluation of this material for the manufacture of nitric acid or a fertilizer, the nitrate being reduced to ammonia and thus estimated.

We will take up a few of the characteristic substances in which nitrogen estimations are required.

In general nitrogen is more accurately and easily measured as ammonia, to which form it is converted by reduction methods. Large amounts are determined by titration, whereas small amounts are estimated colorimetrically. The nitrometer method for determining nitrates (including nitrites), and the free acid in mixed acids, is generally used by manufacturers of explosives.

## DETECTION

**Element. Organic Nitrogen.** — Organic matter is decomposed by heating in a Kjeldahl flask with concentrated sulphuric acid as described under Preparation and Solution of the Sample. Ammonia may now be liberated from the sulphate and so detected.

**Nitrogen in Gas.** — Recognized by its inertness towards the reagents used in gas analysis. The element may be recognized by means of the spectroscope.

**Ammonia.** — Free ammonia is readily recognized by its characteristic odor. A glass rod dipped in *hydrochloric acid* and held in fumes of ammonia produces a white cloud of ammonium chloride, $NH_4Cl$.

*Moist red litmus paper* is turned blue by ammonia. Upon heating the paper the red color is restored, upon volatilization of ammonia (distinction from fixed alkalies).

*Nessler's Test.* — Nessler's reagent added to a solution containing ammonia, combined or free, produces a brown precipitate, $NHg_2I.H_2O$. If the ammoniacal solution is sufficiently dilute a yellow or reddish-brown color is produced, according to the amount of ammonia present. The reaction is used in determining ammonia in water.

**Salts of ammonia** are decomposed by heating their solutions with a strong base such as the hydroxides of the fixed alkalies or the alkaline earths. The odor of ammonia may now be detected.

**Nitric Acid.** *Ferrous Sulphate Test.* — About 1 to 2 cc. of the concentrated solution of the substance is added to 15 to 20 cc. of strong sulphuric acid in a test-tube. After cooling the mixture, the test-tube is inclined and an equal volume of a saturated solution of ferrous sulphate is allowed to flow slowly down over the surface of

the acid. The tube is now held upright and gently tapped. In the presence of nitric acid a brown ring forms at the junction of the two solutions.

The test for nitrate may be made according to the quantitative procedure given for determining nitric acid. It should be remembered that ferrous sulphate should be present in excess, otherwise the brown color is destroyed by the free nitric acid. Traces of nitric acid in sulphuric produce a pink color with the sulphuric acid solution of ferrous sulphate.

Ferro and ferricyanides, chlorates, bromides and bromates, iodides and iodates, chromates and permanganates interfere.

**Diphenylamine Tests for Nitrates.** — $(C_6H_5)_2NH$ dissolved in sulphuric acid is added to 2 or 3 cc. of the substance in solution on a watch-glass. Upon gently warming a blue color is produced in presence of nitrates. Nitric acid in sulphuric acid is detected by placing a crystal of diphenylamine in 3 or 4 cc. of the acid and gently warming. $Cl'$, $Cl^{v}$, $Br^{v}$, $I^{v}$, $Mn^{vii}$, $Cr^{vi}$, $Se^{iv}$, $Fe'''$ interfere.

**Copper** placed in a solution containing nitric acid liberates brown fumes.

**Detection of Nitrous Acid.** — *Acetic Acid Test.* — Acetic acid added to a nitrite in a test-tube (inclined as directed in the nitric acid test with ferrous sulphate), produces a brown ring. Nitrates do not give this. If potassium iodide is present in the solution, free iodine is liberated. The free iodine is absorbed by chloroform, carbon tetrachloride or disulphide, these reagents being colored pink. Starch solution is colored blue.

Nitrous acid reduces iodic acid to iodine. The iodine is then detected with starch, or by carbon disulphide, or carbon tetrachloride.

**Potassium Permanganate Test.** — A solution of the reagent acidified with sulphuric acid is decolorized by nitrous acid or nitrite. The test serves to detect nitrous acid in nitric acid. Other reducing substances must be absent.

### Detection of a Nitrate in a Nitrite Salt

Iridium salts are colored blue by $HNO_3$ but no color is produced by $HNO_2$. Use a 0.025 % solution of $IrO_2$ or $(NH_4)_2\,IrCl_6$ per 100 cc. of 98–99 % $H_2SO_4$ and heat to boiling. The solution should be kept in a stoppered bottle. Into the hot reagent in a test tube is dropped the solid substance tested. A blue color is produced by nitrates. If the nitrite is in solution, make alkaline with KOH, evaporate to dryness and test the residue. Chlorine interferes, but not $FeCl_3$.

## PROCEDURES FOR THE DETERMINATION OF COMBINED NITROGEN

### Ammonia

The volumetric procedures for determination of ammonia are preferred to the gravimetric on account of their accuracy and general applicability. The following gravimetric method may occasionally be of use:

### Gravimetric Determination of Ammonia by Precipitation as Ammonium Platinochloride, $(NH_4)_2PtCl_6$

Ammonia in ammonium chloride may be determined gravimetrically by precipitation with chlorplatinic acid. The method is the reciprocal of the one for determining platinum.

**Procedure.** — The aqueous solution of the ammonium salt is treated with an excess of chlorplatinic acid and evaporated on the steam bath to dryness. The residue is taken up with absolute alcohol, filtered through a weighed Gooch crucible, and washed with alcohol. The residue may now be dried at 130° C. and weighed as $(NH_4)_2PtCl_6$, or it may be gently ignited in the covered crucible until ammonium chloride has been largely expelled and then more strongly with free access of air. The residue of metallic platinum is weighed. If the ignition method is to be followed, the ammonium platinic chloride may be filtered into a small filter, the paper with the washed precipitate placed in a porcelain crucible and then gently heated until the paper is charred (crucible being covered) and then more strongly with free access of air until the carbon has been destroyed.

Factors. $(NH_4)_2PtCl_6 \times 0.2400 = NH_4Cl$, or $\times 0.08095 = NH_4$, or $\times 0.0767 = NH_3$. $Pt \times 0.5453 = NH_4Cl$, or $\times 0.1839 = NH_4$, or $\times 0.1736 = NH_3$.

## NITRIC ACID. NITRATES

The alkalimetric method for determining free nitric acid is given in the chapter on Acids. Special procedures for determining the combined acid are herein given.

### Gravimetric Method for Determining Nitric Acid by Precipitation as Nitron Nitrate, $C_{20}H_{16}N_4.HNO_3$

As in case of ammonia the volumetric methods are generally preferable for determining nitric acid, combined or free. Isolation of nitric acid by precipitation as nitron nitrate may occasionally be used. The fairly insoluble, crystalline compound, $C_{20}H_{16}N_4.HNO_3$ is formed by addition of the base diphenyl-endoanilo-hydro-triazole (nitron) to the solution containing the nitrate.

Such an amount of the substance is taken as will contain about 0.1 gram of nitric acid, and dissolved in about 100 cc. of water with addition of 10 drops of dilute sulphuric acid. The solution is heated nearly to boiling and about 12 cc. of nitron acetate solution added (10 grams of nitron in 100 cc. of 5% acetic acid. The solution is cooled and placed in an ice pack for about two hours, and the compound then transferred to a Gooch or Munroe crucible (weighed crucible if gravimetric method is to be followed), and after draining, it is washed with about 10 to 12 cc. of ice-water added in small portions.

The precipitate washed with ice-water is dried to constant weight at 110° C. 16.53% of the compound is $NO_3$.

Notes. The base diphenyl-endo-anilo-hydro-triazole (nitron) also precipitates the following acids: nitrous, chromic, chloric, perchloric, hydrobromic, hydriodic, hydroferro- and hydroferricyanic, oxalic, picric and thiocyanic acids. Hence these must be absent from the solution if precipitation of nitric acid is desired for quantitative estimation.

**Removal of Nitrous Acid.** — Finely powdered hydrazine sulphate is dropped into the concentrated solution. (0.2 gram of substance per 5 or 6 cc.)

**Chromic acid** is reduced by addition of hydrazine sulphate.

**Hydrobromic acid** is decomposed by chlorine water added drop by drop to the neutral solution, which is then boiled until the yellow color has disappeared.

**Hydriodic acid** is removed by adding an excess of potassium iodate to the neutral solution and boiling until the iodine is expelled.

Solubility of less soluble nitron salts in 100 cc. of water. Nitron nitrate = 0.0099 gram, nitron bromide = 0.61 gram, iodide = 0.017 gram, nitrite = 0.19 gram, chromate = 0.06 gram, chlorate = 0.12 gram, perchlorate = 0.008 gram, thiocyanate = 0.04 gram.

## DETERMINATION OF NITRIC NITROGEN IN SOIL EXTRACTS

### Vamari-Mitscherlich-Devarda Method

**Procedure.** — Forty cc. of water, a small pinch of magnesia and one of magnesium sulphate are added to flask *D* of the Mitscherlich apparatus (Fig. 90). Twenty-five cc. of standard acid and 60 cc. of neutral redistilled water are placed in flask *F;* 250 or 300 cc. of aqueous soil extract are placed in a 500 cc. Kjeldahl flask, 2 cc. of 50% sodium hydroxide added, the mouth of the flask closed with a small funnel to prevent spattering, and the contents of the flask

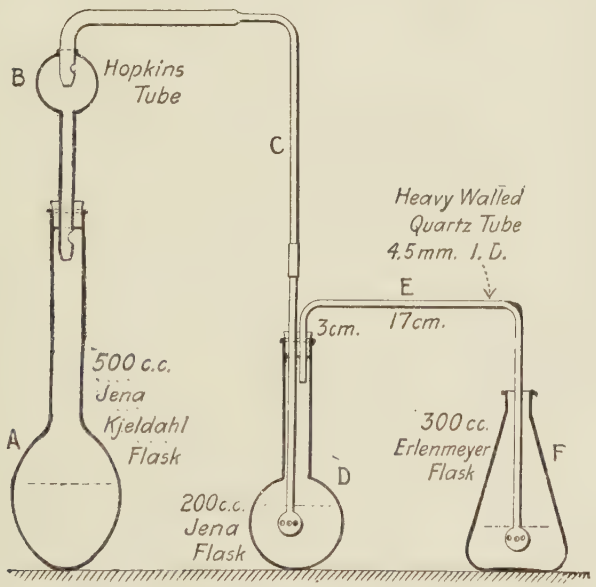



Fig. 90. Mitscherlich's Apparatus for Nitrogen Determination.

boiled for thirty minutes. The water which has boiled off is replaced, and, after cooling, 1 gram of Devarda's alloy (60 mesh), and a small piece of paraffin are added and the flask connected with the apparatus; reduction and distillation are carried on for forty minutes. The receiver contents are then cooled, 4 drops of 0.02% solution of methyl red added, the excess acid nearly neutralized, the liquid boiled to expel $CO_2$, cooled to 10° to 15° and the titration completed.

B. S. Davisson[1] recommends an improved form of scrubber, shown in Fig. 91, to be used in place of the Hopkins tube (Fig. 90). The bulb and adaptor are made of Pyrex glass. Steam condenses in the bulb and the condensate acts as a scrubber, preventing alkali mist from being carried over

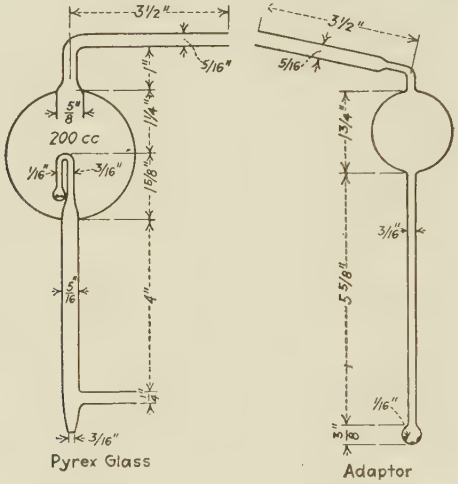



Fig. 91. Davisson's Scrubber.

with the ammonia. During the test ammonia is completely volatilized into the absorption flask. The bulb of the adaptor prevents back suction into the distillation flask.

[1] Reference B. S. Davisson, Ohio, Ag. Exp. Station, J. Ind. Eng. Chem., 11, 465 (May, 1919).

## DETERMINATION OF NITROGEN OF NITRATES (AND NITRITES) BY MEANS OF THE NITROMETER

The nitrometer is an exceedingly useful instrument employed in the accurate measurement of gases liberated in a great many reactions and has therefore a number of practical applications. It may be used in the determination of carbon dioxide in carbonates; the available oxygen in hydrogen dioxide; in the valuation of nitrous ether and nitrites; in the valuation of nitrates and nitric acid in mixed acids.

The method for the determination of nitrogen in nitrates, with which we are concerned in this chapter, depends on the reaction between sulphuric acid and nitrates in presence of mercury:

$$2KNO_3 + 4H_2SO_4 + 3Hg = K_2SO_4 + 3HgSO_4 + 4H_2O + 2NO.$$

The simplest type of apparatus is shown in the illustration, Fig. 92. The graduated decomposition tube has a capacity of 100 cc. It is connected at the base by means of a heavy-walled rubber tubing with an ungraduated leveling tube (*b*). At the upper portion of (*a*) and separated from it by a glass stop-cock (*s*) is a bulb (*c*) of about 5 cc. capacity; a second stop-cock enables completely enclosing the sample, as may be necessary in volatile compounds. The glass stop-cock (*s*), directly above the graduated chamber, is perforated so as to establish connection with the tube (*d*) when desired and the graduated cylinder (*a*).

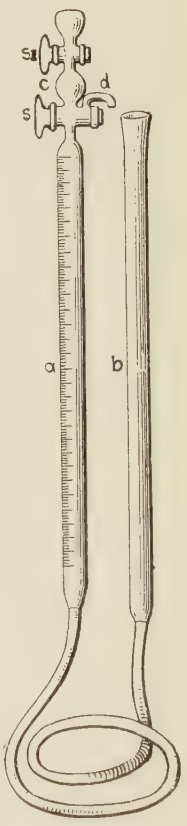


Fig. 92. Nitrometer.

**Procedure.** — The tube (*b*) is filled with mercury and the air in (*a*) now displaced by mercury, by turning the stop-cock to form an open passage between (*a*) and (*d*) and then raising (*b*). A sample of not over 0.35 gram of potassium nitrate or a corresponding amount of other nitrates, is introduced into (*c*), the material being washed in with the least amount of water necessary (1 to 2 cc.). By lowering (*b*) and opening the stop-cock *s* the solution is drawn into the decomposition chamber, taking care that no air enters. This is followed by about 15 cc. of pure, strong sulphuric acid through $s_1$ and *s*, avoiding admitting air as before. NO gas is liberated by the heat of reaction between the sulphuric acid and the water solution. When the reaction subsides, the tube (*a*) is shaken to mix the mercury with the liquor and the NO completely liberated. The gas is allowed to

cool to room temperature and then measured, after raising or lowering (*b*) so that the column of mercury is the calculated excess of height above that in (*a*) in order to have the gas under atmospheric pressure. The excess of height is obtained by dividing the length of the acid layer in (*a*), in millimeters, by 7 and elevating the level of the mercury in (*b*) above that in (*a*) by this quotient; i.e., if the acid layer = 21 mm. the mercury in (*b*) would be 3 mm. above that in (*a*). The volume of gas is reduced to standard conditions by using the formula

$$V' = \frac{V(P - w)}{760(1 + 0.00367t)}$$

$V'$ = volume under standard conditions; $V$ = observed volume; $P$ = observed barometric pressure in mm.; $w$ = tension of aqueous vapor at the observed temperature, expressed in millimeters; $t$ = observed temperature.

One cc. gas = 4.62 milligrams of $KNO_3$, or 3.8 milligrams of $NaNO_3$ or 2.816 milligrams of $HNO_3$.

## DETERMINATION OF NITRITES

### GRAVIMETRIC METHOD OF BUOVOLD[1]

One and one fourth to 1.5 gram of $AgBrO_3$ is dissolved in 100 cc. of water and 110 cc. of 2 N. acetic acid, in an Erlenmeyer flask. 200 cc. of the nitrite solution (1 g. $NaNO_2$) are added from a burette, stirring the mixture during addition of the nitrite. A pale green precipitate is obtained. 30 cc. of $H_2SO_4$ (1 : 4) are added, the mixture warmed to 85°C. When the yellow precipitate settles it is filtered on a Gooch and washed with hot water, then dried and weighed as AgBr + AgCl. Chlorine is determined on a separate portion and AgCl deducted. AgBr × 0.9070 = $NaNO_2$. The method is specially applicable to nitrites high in chlorine.

### VOLUMETRIC PERMANGANATE METHOD

**Principle.** — Potassium permanganate reacts with nitrous acid or a nitrite as follows:

$$5N_2O_3 + 4KMnO_4 + 6H_2SO_4 = 5N_2O_5 + 2K_2SO_4 + 4MnSO_4 + 6H_2O.$$

$$5HNO_2 + 2KMnO_4 + 3H_2SO_4 = 5HNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

Since $2KMnO_4$ in acid solution has five available oxygens for oxidation of substances (i.e., $2KMnO_4 = K_2O.2MnO + 5O$ equivalent to 10H) the molecular weights of the constituents divided by 20 in the first equation and by 10 in the second would represent the normal weights per liter, e.g., $5N_2O_3$ divided by 20 = 76 divided by 4 = 19 grams $N_2O_3$ per liter. $4KMnO_4$ divided by 20 or $2KMnO_4$ divided by 10 = 158.03 divided by 5 = 31.61 grams of $KMnO_4$ per liter for a normal solution. In the second equation if Na represents the univalent element we would have $5NaNO_2$ divided by 10 or 69 divided by 2 = 34.5 grams per liter. Hence 1 cc. of a normal $KMnO_4$ solution would oxidize 0.019 gram $N_2O_3$ or 0.0345 gram of $NaNO_2$ to form $N_2O_5$ and $NaNO_3$ respectively.

Organic matter is also oxidized by $KMnO_4$ hence will interfere if present.

#### Special Reagents

**N/5 Sodium Oxalate.** — $Na_2C_2O_4$ reacts with $KMnO_4$ as follows:

$$5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 10CO_2 + 8H_2O$$

Hence $5Na_2C_2O_4$ divided by 10 or 134 divided by 2 = 67 grams per liter = a normal sodium oxalate solution. A N/5 solution requires 13.4 grams $Na_2C_2O_4$ per liter.

[1] Chem. Ztg. 38, 28; C. A. 8, 1250 (1914).

**N/5 Potassium Permanganate.** — The solution contains 6.322 grams $KMnO_4$ per liter.

**Preparation of the Sample. Soluble Nitrites.** — Ten grams of the nitrite are dissolved in water and made to 1000 cc.; 10 cc. contain 0.1 gram of the sample.

**Water-insoluble Nitrites.** — 0.5 to 1.0 gram of the nitrite according to the amount of nitrous acid present is taken for analysis. An excess of $KMnO_4$ solution is added, followed by dilute $H_2SO_4$ and the excess standard permanganate titrated with sodium oxalate according to directions given under Procedure.

**Nitrous Acid in Nitric Acids and Mixed Acids.** — This is present generally in very small amounts so that a large sample is taken. The amount and details of the procedures are given under the special subject.

For routine work where a number of daily determinations are made, a 50 cc. burette is generally preferred.

**Trial Run.** — If the approximate strength of the salt is not known the following test may be quickly made to ascertain whether more than 50 cc. of solution is necessary and the approximate amount of $KMnO_4$ required for oxidation.

Ten cc. of the solution together with 100 cc. of water are placed in a 4 in. casserole and about 10 cc. of dilute $H_2SO_4$, 1 : 1, added. Standard $KMnO_4$ from a 50 cc. burette is now run into the sample until a permanent pink color is obtained. The cc. of $KMnO_4$ multiplied by 5 = the approximate amount of permanganate solution required for oxidation of 50 cc. of sample. An excess of 5 to 10 cc. should be taken in the regular run.

**Titration of Nitrite.** — Sufficient standard N/5 $KMnO_4$ to oxidize the sample to be titrated (as ascertained by the trial run) and 10 cc. excess are placed in a casserole. The solution is acidified with 10 cc. of dilute (1 : 4) $H_2SO_4$ and 50 cc. of the nitrite solution is added slowly with constant stirring. The sample is placed on a hot plate until the mixture reaches a temperature of 70° to 80° C. and 25 cc. more of the dilute $H_2SO_4$ added. The excess permanganate is now titrated with N/5 $Na_2C_2O_4$, the oxalate being added slowly until the permanganate color is destroyed. Five cc. excess of the oxalate are added and the exact excess determined by titrating the hot solution with N/5 $KMnO_4$ to a faint pink color. The total permanganate solution taken minus the oxalate titration = cc. $KMnO_4$ required by the nitrite.

Standard ferrous sulphate, $FeSO_4$, may be used, in place of sodium oxalate. The titration then may be conducted in the cold.

One cc. of N/5 $KMnO_4$ = 0.0038 g. of $N_2O_3$, or 0.0069 g. of $NaNO_2$, or 0.0085 g. of $KNO_2$.

## OSMIUM [1]

**Element, Osmium. Os. at.wt. 190.9; sp.gr. 22.4; m.p. 2700° C.? oxides, OsO, $Os_2O_3$, $OsO_2$, $OsO_4$.**

Osmium is estimated mainly in osmiridium and platinum residues.

### DETECTION

Osmium occurs with platinum ores as a natural alloy with iridium (Osmiridium), and remains undissolved in the form of hard, white metallic-looking grains when the ores are treated with aqua regia. The chlorides, $OsCl_2$ and $OsCl_4$, combine with the alkali chlorides. Through the action of $HNO_3$, aqua regia or heating in a stream of moist chlorine, osmic tetroxide is formed. Osmium is very volatile and the fumes are poisonous. It is detected readily by the odor when heated, as the fumes are highly corrosive and disagreeable like chlorine. Chlorine passed over hot osmium mixed with KCl gives $K_2OsCl_6$, which dissolves in cold water.

The oxy-hydrogen flame volatilizes the metal but does not melt it. When strongly heated in contact with air, the finely divided osmium burns and is converted into $OsO_4$ commonly called osmic acid.

Osmium monoxide, OsO, is obtained when the corresponding sulphite mixed with sodium carbonate is ignited in a current of carbon dioxide. It is a grayish-black powder insoluble in acid.

The oxide, $Os_2O_3$, is a black insoluble powder obtained by heating its salts with sodium carbonate in a current of carbon dioxide.

Osmium dioxide, $OsO_2$, is obtained from its salts in a similar way to the foregoing oxides. It is likewise formed when its hydroxide is heated in a current of carbon dioxide.

Osmium tetroxide, $OsO_4$. Very finely-divided metallic osmium oxidizes slowly at the ordinary temperature, and at about 400° takes fire with formation of $OsO_4$. The denser the metal the higher is the temperature needed for oxidation.[1]

**Hydrogen sulphide** precipitates dark brown osmium sulphide, $OsS_2$, but only in the presence of strong mineral acid; from an aqueous solution of osmic acid there forms a dark brownish-black sulphide $OsS_4$. These are insoluble in ammonium sulphide.

**Potassium hydroxide** precipitates reddish-brown osmium hydroxide, $Os(OH)_4$.

**Ammonium hydroxide** precipitates the osmium hydroxide.

**Zinc and formic acid** precipitate black metallic osmium.

**Hydrogen** reduces osmium compounds to the metal.

[1] For occurrence see Platinum.

**Potassium nitrate** added to a solution of osmic acid reduces it to osmous acid which unites with an alkali forming a beautiful red salt.

**Sodium sulphite** yields a deep violet coloration and a dark blue osmium sulphite separates out gradually.

**Phosphorus** reduces osmium from an aqueous solution.

**Mercury** precipitates osmium from an aqueous solution of osmic acid mixed with HCl.

**Stannous chloride** produces a brown precipitate, soluble in HCl to a brown fluid.

## GRAVIMETRIC METHODS FOR THE DETERMINATION OF OSMIUM [1]

The osmium is very difficult to ascertain on account of the element being very volatile.

After the platinum is extracted the residue or osmiridium is mixed with two or three times its weight of common table salt. The mixture is put in a porcelain or silica tube and heated to a dull-red heat; moist chlorine is then passed through the tube and thence through receivers containing KOH and $C_2H_5OH$ to catch the Os and Ru that pass over. The mass is cooled and dissolved with water. After several treatments the entire group of platinum metals will be in solution.

The osmium material may also be fused with KOH and $KNO_3$ and the melt dissolved in water. The osmium will be in solution as potassium osmate, $K_2OsO_4$, while the iridium remains as residue.

The potassium osmate, $K_2OsO_4$, solution is put in a small retort, and boiled with $HNO_3$, the $OsO_4$, is conducted into receivers containing NaOH solution and $C_2H_5OH$. After acidifying with a little HCl the osmium can be precipitated with $Na_2S_2O_3$ as a brown precipitate of $OsO_4$ which is filtered, washed, dried and weighed as the oxide, or reduced in hydrogen and weighed as the metal. The osmate solution from the receivers above is heated gently and strips of aluminum are plunged in; the osmium will be deposited in metallic form, while the aluminum dissolves in the soda. Care must be taken not to add too much aluminum, as an aluminate might be precipitated which is troublesome. When the solution is discolored the dense precipitated osmium is washed by decantation with water to remove the sodium aluminate, and then with 5% $H_2SO_4$ solution to remove the excess aluminum. The osmium is dried in a bell-jar filled with hydrogen, then heated to a dull redness and cooled in a current of hydrogen. The osmium is weighed as the metal. As a check the osmium may be driven off in the form of $OsO_4$ by heating to redness with plenty of air, or better, in a current of oxygen and weighing again.[2]

The osmate solution from the condensing receivers or from the fusion of KOH and $KNO_3$ containing the ruthenium and osmium is placed in a retort and HCl is added. A slow current of air or oxygen is passed through the retort and thence through receivers containing KOH and alcohol similar to the ones mentioned above. These receivers are kept as cold as possible. The osmium is distilled over as $OsO_4$ while the ruthenium remains in the retort. Combine the solutions in the receivers and proceed to determine the osmium as described above.

[1] Chapter contributed by Mr. R. E. Hicksman, chief chemist of J. Bishop & Co. Platinum Works.

[2] "Select Methods of Chemical Analysis," Sir Wm. Crookes.

The potassium or sodium osmate solution from the receivers above or where osmium tetroxide is dissolved in potassium hydroxide solution and alcohol is heated at 40 or 50° to form potassium osmate. A slight excess of dilute sulphuric acid is added and then 10 cc. more of alcohol in order to prevent reoxidation. After ten or twelve hours, a bluish-black deposit settles, while the supernatant liquid is colorless and free from osmium. The precipitate is filtered, washed with aqueous alcohol, and converted into metallic osmium by reduction in a current of hydrogen.[1]

[1] "Journal London Chemical Society Abstracts," 1907, by Carl Paal and Conrad Amberger.

## OXYGEN

**Properties.** — at.wt. 16; colorless, odorless, tasteless gas; b.p. −182° C. (liquid sp.gr. 1.12); 1 liter weighs 1.429 g., 1 liter of air weighs 1.293 g., hence oxygen weighs 1.105 times air. Oxygen combines with all the elements with the exception of fluorine and the elements of the argon group.

### OCCURRENCE

The element occurs free in air (21 percent by volume of air). It is found combined forming oxides; combined with hydrogen it forms water; it occurs in form of oxide with a great many minerals. It is estimated that half our globe is made up of oxygen.

### DETERMINATION OF OXYGEN IN STEEL

The properties of steel are affected by the presence of oxygen so that its determination is being recognized as an essential one in the analysis of this product. It occurs in steel as occluded oxygen and as

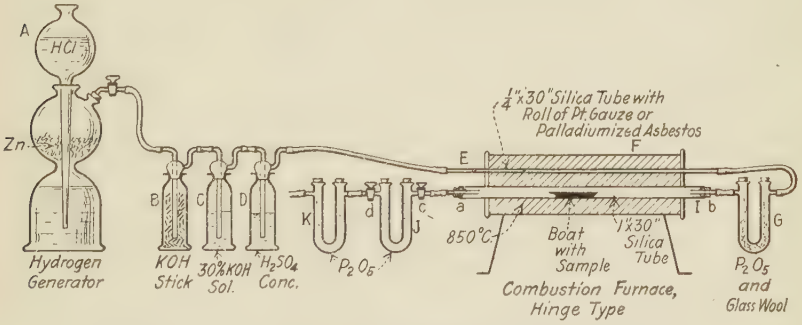



Fig. 93. — Apparatus for Determining Oxygen in Steel.

combined oxygen i.e. oxides of iron, aluminum, manganese, silicon, titanium, etc. The following method determines the occluded oxygen and the oxygen combined with iron, but does not determine that combined with manganese, aluminum and silicon, as these oxides are not reduced by hydrogen.

The method depends upon the combination of hydrogen with the oxygen of iron when the latter is heated in a current of hydrogen; the water formed is absorbed and weighed and the oxygen calculated.

The apparatus shown in Fig. 93 gives full details. It is shown that hydrogen generated by the action of HCl on zinc is purified by passing through the wash bottles *B*, *C*, *D*, containing KOH and $H_2SO_4$, oxygen in the gas is removed by passing through a preheated tube containing platinum gauze or palladiumized asbestos, the water formed being absorbed in the $P_2O_5$ in *G*. The pure hydrogen now combines with the oxygen of the sample and the water formed is absorbed in $P_2O_5$ in the tube *J*.

**Procedure.** *Preliminary.* — The apparatus is connected up as shown in Fig. 93 and hydrogen gas passed through for 5 to 10 minutes. The $P_2O_5$ tube is now weighed as in regular test (see notes), the tube being disconnected from *K*, which is used as a guard to prevent moisture being absorbed by an accidental back suction of air.

The sample of 20 to 30 grams of the steel borings are placed in a nickel boat ($\frac{1}{2}'' \times \frac{1}{2}'' \times 6''$) and this inserted quickly through the opening at " a " into the combustion tube, the current of hydrogen flowing through the tube. The absorption tube *J* and its guard are connected up and the heat turned on. (All connections should be air tight.) The temperature of bright-red heat (850° C.) is desired. The hydrogen is passed at a rate of about 100 cc. per minute, the rate having been previously established by the speed of bubbles in *D*. After 30 minutes the heat is turned off, the top of the hinged furnace lifted, and the tube raised and allowed to cool, hydrogen gas still passing. A blast of air assists the cooling.

The cocks " c " and " d " of *J* are turned off in the order named, the exit end of the guard *K* closed and the two connected placed in the balance for about 10 minutes. The exit end of the guard is now opened, the cock " d " quickly opened and shut, thus obtaining atmospheric pressure in the tube *J* without intake of air. The guard is now disconnected and *J* is weighed. The increase of weight due to absorbed water is multiplied by 0.889 to obtain the weight of occluded oxygen and the oxygen combined with iron.

Notes. The tube *J* is weighed before and after the test filled with hydrogen under atmospheric pressure and at the same temperature, so that it is not necessary to aspirate air through the tube as is sometimes recommended. The preliminary run for obtaining the initial weight should be conducted under conditions the same as in the final test, the tubes *J* and *K* being closed, transferred to the balance and *J* finally weighed as stated at the end of the procedure, so that the conditions will be the same in regard to the inclosed hydrogen or the tube.

The $P_2O_5$ tubes are charged by packing alternate layers of $P_2O_5$ and glass wool, beginning and ending with the latter, otherwise the powder will pack and prevent the passage of gas.

The drilling of the samples should be done slowly to prevent heating, the drills being free of grease or oil. The samples should be taken from several sections of the ingot, whose surface has been cleaned by a cutting tool or by emery.

The apparatus should be tested for leaks as described in the notes in the chapter on Hydrogen.

### DETERMINATION OF FREE OXYGEN IN GAS

**(1) By Phosphorus.** — 100 cc. of gas are measured out as with the Orsat apparatus, the burette being allowed to drain two minutes. The rubber connectors upon the burette and pipette are filled with water, the capillary tube inserted, as far as it will go, by a twisting motion, into the connector upon the burette, thus filling the capillary with water; the free end of the capillary is inserted into the pipette

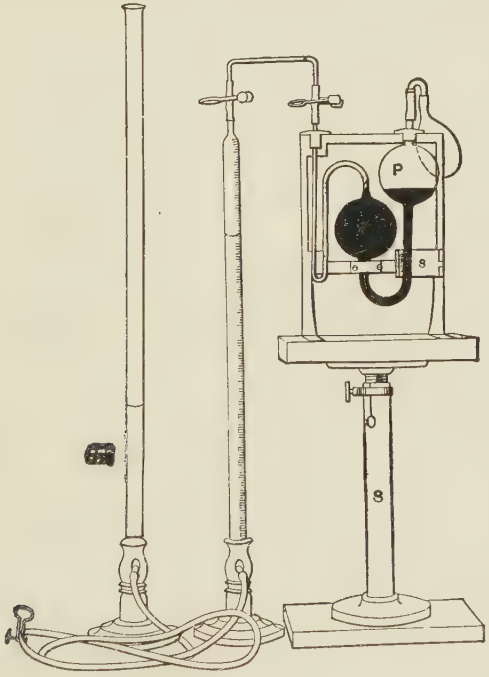



Fig. 94

connector, the latter pinched so as to form a channel for the water contained in it to escape, and the capillary twisted and forced down to the pinchcock. There should be as little free space as possible between the capillaries and the pinchcock. Before using a pipette, its connector (and rubber bag) should be carefully examined for leaks, especially in the former, and if any found the faulty piece replaced.

The pinchcock on the burette and pipette are now opened, the gas forced over into the phosphorus, and the pinchcock on the pipette closed; action immediately ensues, shown by the white fumes; after allowing it to stand fifteen minutes the residue is drawn back into

the burette, the latter allowed to drain and the reading taken. The absorption goes on best at 20° C., not at all below 15° C.; it is very much retarded by small amounts of ethane and ammonia. It cannot be used to absorb commercial oxygen. No cognizance need be taken of the fog of oxides of phosphorus.

(2) **By Pyrogallate of Potassium.**[1] — 100 cc. of gas[2] are measured out as before, the carbon dioxide absorbed with potassium hydrate and the oxygen with potassium pyrogallate, as with Orsat apparatus; before setting aside the pyrogallate pipette, the number of cubic centimeters of oxygen absorbed should be noted upon the slate *s* on the stand. This must never be omitted with any pipette save possibly that for potassium hydroxide, as failure to do this may result in the ruin of an important analysis. The reason for the omission in this case is found in the large absorption capacity — four to five liters of carbon dioxide — of the reagent.

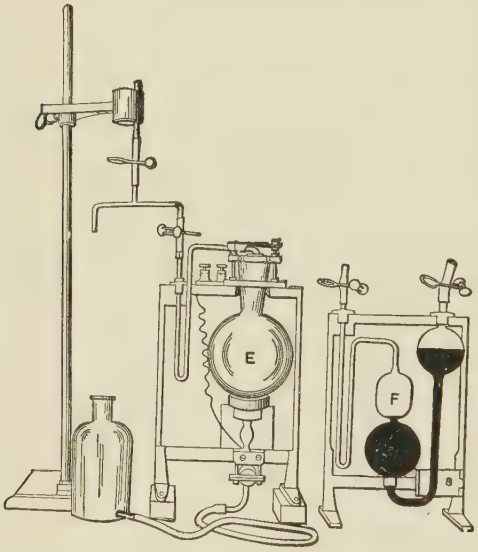



Fig. 95 Explosion Pipette

(3) **By Explosion with Hydrogen.** — Forty-three cc. of gas and 57 cc. of hydrogen are measured out, passed into the small explosion pipette, the capillary of the pipette filled with water, the pinchcocks and glass stopcock all closed, a heavy glass or fine wire gauze screen placed between the pipette and the operator, the spark passed between the spark wires, and the contraction in volume noted. *The screen should never be omitted, as serious accidents may occur thereby.* The oxygen is represented by one-third of the contraction. For very accurate work the sum of the combustible gases should be but one-sixth that of the non-combustible gases, otherwise some nitrogen will burn and high results will be obtained;[3] that is, $(H + O) : (N + H) :: 1 : 6$.

[1] See Anderson's work, J. Ind. and Chem., 7, 587, 1915.

[2] A. H. Gill finds after an experience of more than twenty-five years in the laboratory with hundreds of students, that sodium pyrogallate can be used with practically the same results as the potassium compound. The absorption is complete, as shown by subsequent treatment with cuprous chloride.

[3] This is shown in the work of Gill and Hunt, J. Am. Chem. Soc., 17, 987, 1895.

## PALLADIUM [1]

**Element, Palladium. Pd. at.wt. 106.7; sp.gr. 11.9; m.p. 1549° C.; oxides, PdO, $PdO_2$.**

Palladium is determined in alloys, ores, jeweler sweepings, etc.

### DETECTION

This metal is also found associated with platinum and iridium as well as ruthenium, rhodium, and osmium. It occurs in the metallic state sometimes with gold and silver. It resembles platinum as to lustre and color. Palladium sponge when heated slightly gives a rainbow effect due to the formation of oxides. Hydrogen passed over the sponge restores it to the original color. It dissolves in $HNO_3$ and boiling $H_2SO_4$. HCl has little action upon it. It is readily soluble in aqua regia, forming $PdCl_2$. $PdCl_4$ is unstable.

Palladium monoxide, PdO, is formed by a long-continued heating of the spongy metal in a current of oxygen at a temperature from 700 to 840° C or by heating a mixture of a palladium salt with potassium carbonate. The pure hydrated oxide is best prepared by the hydrolysis of the nitrate.

It acts as a powerful oxidizing agent to organic substances, and is reduced to metal by hydrogen peroxide.

Palladium dioxide, $PdO_2$, is obtained in an impure hydrated form as a brown precipitate by the addition of caustic soda to potassium palladichloride. This is soluble in acids, but becomes less soluble when preserved. It can be obtained free from alkali and basic salts by the anodic oxidation of the nitrate, but it is not quite free from monoxide. The dioxide very readily decomposes into the monoxide and oxygen, and cannot be obtained in the anhydrous state. It acts as a vigorous oxidizing agent and decomposes hydrogen peroxide.

**Alkalies** precipitate in a concentrated solution a dark-brown precipitate soluble in an excess of the reagent. If boiled a brown palladous hydroxide is precipitated. The anhydrous oxide is black.

**Ammonia** added to a concentrated solution gives a flesh-red precipitate, $PdCl_2.NH_3$, soluble in excess of ammonia. If HCl is added to this solution the yellow compound of pallad-ammonium chloride, $Pd(NH_3Cl)_2$, is deposited.

**Sulphur dioxide** precipitates the metal from the nitrate or sulphate solution but not from the chloride.

**Cuprous chloride** precipitates the metal from the sulphate, nitrate and chloride solution when they are not too strongly acid.

[1] For occurrence see Platinum.

**Mercuric cyanide** precipitates a yellowish-white gelatinous precipitate, $Pd(CN)_2$, insoluble in dilute acids, but dissolving in ammonia and in potassium cyanide to $K_2Pd(CN)_4$.

**Potassium iodide** precipitates black palladous iodide, $PdI_2$, insoluble in water, alcohol, and ether, but soluble in an excess of reagent.

**Hydrogen sulphide** precipitates black palladous sulphide, PdS, soluble in HCl and aqua regia, but insoluble in $(NH_4)_2S$.

**Potassium nitrite** precipitates a yellow crystalline powder, $K_2Pd(NO_2)_4$.

**Ferrous sulphate** slowly produces a black precipitate of metallic palladium from the nitrate.

**Ammonium chloride** precipitates palladium as $(NH_4)_2PdCl_4$ from the nitrate.

**Formic acid, zinc and iron** reduce to metallic palladium.

**Soluble carbonates** precipitate brown palladous hydroxide, $Pd(OH)_2$, soluble in excess, and reprecipitated on boiling.

## GRAVIMETRIC METHODS FOR THE DETERMINATION OF PALLADIUM

### Preparation and Solution of the Sample

The solubility of palladium has been taken up under Detection. Palladium when alloyed with platinum, or an alloy of platinum, iridium and palladium, dissolves with the other metals in aqua regia as the chloride. When palladium is alloyed with silver the palladium and silver are dissolved in $HNO_3$, from which the silver can be separated.

**Separation of Palladium from Platinum and Iridium.** — The chlorides of palladium, platinum and iridium in solution must be free from $HNO_3$. The platinum and the iridium are precipitated with $NH_4Cl$ leaving the palladium in solution. The precipitate is put on a filter and washed free from Pd with $NH_4Cl$ solution and alcohol.

**Separation of Palladium from Silver and Gold.** — At least three times the weight of the gold in silver should be present in the alloy in order to separate the silver and palladium from the gold. The silver and the palladium will dissolve in $HNO_3$, leaving the gold as the residue. This is filtered off and the silver may be precipitated with HCl. The silver chloride is filtered off and washed with hot water acidulated with HCl until free from palladium. Since AgCl tends to retain palladium it is advisable to redissolve the silver with $HNO_3$ after reduction of AgCl and reprecipitate the chloride to obtain a complete separation of palladium.

**Separation of Palladium from Platinum.** — The chlorides of platinum and palladium being free from $HNO_3$ and having an excess of HCl are diluted with water. A 10% solution of potassium iodide is added until all of the palladium is precipitated. Avoid adding a large excess. The precipitate of $PdI_2$ is filtered off and washed free from platinum and alkali with water slightly acidulated with HCl. The filter is ignited to metallic sponge in a current of hydrogen.

## METHODS

1. The palladium is precipitated from the solution by granulated zinc, the solution having a small amount of free hydrochloric acid. The residue, after the zinc is dissolved, is put on a filter and washed free from impurities. Ignite the filter and dissolve in a small amount of aqua regia and evaporate to a syrupy consistency. Dilute with a small amount of water and add a few drops of $HNO_3$; precipitate the palladium with $NH_4Cl$ crystals. Heat for a few minutes and let cool. Filter, wash with alcohol, and ignite. Reduce in hydrogen or moisten with formic acid to reduce to metal any oxide that may have formed. Dry and weigh as metallic palladium.

2. With the solution containing about one-fifth the volume of free HCl, the palladium is precipitated with 10% KI solution. Heat to nearly boiling, filter, wash free from iron, etc., with 1:4 HCl. Ignite, cool, reduce in hydrogen or moisten with formic acid, dry and weigh as metallic Pd.

3. The filtrate from the platinum precipitation or the nearly neutral solution containing the Pd is made to about 150 cc., and the Pd is precipitated by adding a solution of dimethylglyoxime (1% solution in alcohol). Bring to boiling and let stand overnight if convenient. Filter on a weighed Gooch crucible and wash with hot water slightly acidified with HCl, then with alcohol. Dry and weigh as $(C_8H_{14}N_4O_4)Pd$, which contains 31.67% Pd.

4. The nitric acid in the palladium solution is expelled by evaporating with HCl. Neutralize the chloride solution almost completely with sodium carbonate and mix the solution with a solution of mercuric cyanide, $Hg(CN)_2$, and heat gently for some time. Let stand until cool, overnight if convenient. A yellowish-white precipitate of $Pd(CN)_2$ is formed. Filter, wash with 1% $Hg(CN)_2$ solution, ignite and reduce in hydrogen to metal, or reduce with formic acid, dry, and weigh as metallic Pd.

## PHOSPHORUS

$P_4$, at.wt. 31.04: sp.gr. { yellow 1.831 ; red 2.296 } ; m.p. { 44° ; 725° } ; b.p. { 290° C oil, ; oxides, ..... }

$P_2O_5$, $PO_2$, $P_2O_5$; acids, $H_3PO_2$, $H_3PO_3$, $H_3PO_4$, $HPO_3$, $H_4P_2O_7$.

### OCCURRENCE

The determination of the pentoxide of phosphorus is required in a large number of substances, since it is widely distributed in the form of phosphates — calcium phosphate, $Ca_3(PO_4)_2$; fluor apatite, $3Ca_3(PO_4)_2.CaF_2$; chlor apatite, $3Ca_3(PO_4)_2.CaCl_2$; vivianite, $Fe_3(PO_4)_2.8H_2O$; wavellite, $2Al_2(PO_4)_2.Al_2(OH)_6.9H_2O$; pyromorphite, $3Pb_3(PO_4)_2.PbCl_2$; phosphates of iron and calcium in phosphate ores, hence in slags of the blast furnace. It occurs in fertile soils, bones, plant and animal tissues.

**Minerals.** — Among the minerals mentioned above we need mention only the following for commercial importance as phosphates — *Apatite,* Asparagus Stone, Phosphate Rock, $Ca_5(ClF)(PO_4)_3$, a brittle, transparent to opaque, mineral of vitreous to resinous lustre, white, colorless, yellow, green, violet, red and brown color, with white streak. Occurs as small or large hexagonal prisms, or in compact, dull gray or white masses, nodules resembling limestone. Varieties, Phosphorite, Phosphate Rock, Guano. The chief source of phosphates —

*Wavellite,* $Al_6(OH)_6(PO_4)_4.9H_2O$; *Wagnerite,* $Mg_2PO_4F$. *Vivianite,* Blue Iron Earth, $Fe_3(PO_4)_2.8H_2O$.

The chemist is especially concerned in the determination of phosphoric acid ($P_2O_5$), in the evaluation of materials used for the manufacture of the acid — bone ash and phosphate rock (see table below). Generally, determinations of lime, iron and aluminum are also desired and frequently a more complete analysis. In the analysis of phosphoric acid certain impurities occurring in the crude material used are determined, e.g., iron, lime, magnesium, sulphuric, hydrochloric and hydrofluoric acids, etc. Phosphoric acid is determined in the evaluation of phosphate fertilizers, phosphates used in medicine, phosphate baking powders, etc.

The element is determined in iron, steel, phosphor bronzes, and other alloys.

TYPICAL ANALYSES[1]

| Substance | Bone Ash | Charlestown Phosphate | Spanish Phosphorite | Sombrero Phosphate | Redonda Phosphate | Canadian Phosphate |
|---|---|---|---|---|---|---|
| Phosphoric oxide | 39.55 | 27.17 | 33.38 | 35.12 | 35.47 | 37.68 |
| Sulphur trioxide | .... | 3.30 | 0.57 | | | |
| Carbon dioxide | 4.43 — | 4.96 | 4.10 | 7.40 | | |
| Lime | 52.46 | 44.03 | 47.16 | 51.33 | .... | 51.04 |
| Magnesia | 1.02 | 0.37 | trace | | | |
| Alumina | .... | 1.44 | 0.89 | Fe | 20.17 | $Fe_2O_3$, |
| Ferric oxide | 0.17 | 0.43 | 2.59 | 1.02 | 8.85 | $Al_2O_3$, |
| Fluorine, etc. | .... | 2.38 | 4.01 | .... | .... | F. etc |
| Alkaline salts | .... | 0.87 | .... | 0.42 | | 6.88 |
| Silica — sand, etc. | 0.51 | 5.60 | 3.71 | 2.02 | 9.70 | 4.29 |

[1] Thorpe, "Dictionary of Applied Chemistry," Longmans, Green & Co.

## DETECTION

**Element.** — Phosphorus is recognized by its glowing (phosphorescence) in the air. The element is quickly oxidized to $P_2O_5$; if the yellow modification is slightly warm (34° C.) the oxidation takes place with such energy that the substance bursts into flame. The red form is more stable. It ignites at 260° C.

Boiled with KOH or NaOH it forms phosphine, $PH_3$, which in presence of accompanying impurities is inflammable in the air.

Phosphorus oxidized to $P_2O_5$ may be detected with ammonium molybdate, a yellow compound, $(NH_4)_3PO_4.12MoO_3.3H_2O$, being formed.

**Acids.** — *Hypophosphorous Acid,* $H_3PO_2$, heated with copper sulphate to 55° C. gives a reddish-black compound, $Cu_2H_2$, which breaks down at 100° C to H and Cu. Permanganates are reduced immediately by hypophosphorous acid. No precipitates are formed with barium, strontium or calcium solutions. Zinc in presence of sulphuric acid reduces hypophosphorous acid to phosphine, $PH_3$.

*Phosphorous Acid,* $H_3PO_3$. — Copper sulphate is reduced to metallic copper and hydrogen is evolved, no $Cu_2H_2$ being formed as in case of hypophosphorous acid. Permanganates are reduced slowly. Added to solutions of barium, strontium or calcium white phosphites of these elements are precipitated. Alkali phosphites are soluble in water, while hypophosphites are not readily soluble.

*Orthophosphoric Acid,* $H_3PO_4$. — Ammonium phosphomolybdate precipitates yellow ammonium phosphomolybdate from slightly nitric acid solutions. The precipitate is soluble in ammonium hydroxide.

*Metaphosphoric Acid,* $HPO_3$. — Converted by nitric acid in hot solutions to the ortho form. Metaphosphoric acid is not precipitated by ammonium molybdate.

*Pyrphosphoric Acid,* $H_4P_2O_7$. — Converted to orthophosphoric acid in hot solutions by nitric acid. No precipitate is formed with ammonium molybdate.

Comparison of Ortho-, Meta- and Pyrophosphoric Acids

| Reagent | Orthophosphoric acid. | Metaphosphoric acid. | Pyrophosphoric acid. |
|---|---|---|---|
| Ammonium molybdate | Yellow ppt. | No ppt. | No ppt. |
| Albumin | ..... | Coagulated | Not coagulated |
| Zinc sulphate, cold, in excess | ..... | No. ppt. | White ppt. |
| Silver nitrate in neutral solution | Yellow ppt., $Ag_3PO_4$ | White ppt., $AgPO_3$ | White ppt. $Ag_4P_2O_7$ |
| Magnesium salts | White ppt. | No ppt. | No ppt. |

Phosphorous acids are distinguished from phosphoric acids by the phosphine formed with the former when acted upon with zinc.

Acid phosphates are distinguished from normal phosphates as follows: Neutral silver nitrate added to an acid phosphate liberates free nitric acid (Litmus test), the following reaction taking place:

$$3AgNO_3 + Na_2HPO_4 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$

The solution resulting when silver nitrate is added to normal phosphate solution is neutral.

$$3AgNO_3 + Na_3PO_4 = Ag_3PO_4 + 3NaNO_3.$$

## METHODS OF ANALYSIS

**Preliminary Remarks.** Practically all procedures for the determination of phosphorus depend upon its oxidation to ortho phosphoric acid and its precipitation by ammonium molybdate from a nitric acid solution as ammonium phospho-molybdate. It may now be determined either gravimetrically or volumetrically. Two procedures are of importance in the gravimetric determination of phosphorus; the first depends upon the direct weighing of the yellow phosphomolybdate, dried at 110° C.; the second, on the conversion of the yellow precipitate to the magnesium salt and its ignition to pyrophosphate. Two volumetric procedures, which are of special value in the determination of small amounts of phosphorus as in case of phosphorus in iron and steel, are to be recommended for their rapidity and accuracy. One of these is to dissolve the yellow precipitate in a known amount of standard alkali, titrate the excess alkali with standard acid, the difference being the amount combined with ammonium phosphomolybdate. From this the amount of phosphorus present may be calculated. A second procedure of equal accuracy and rapidity is to dissolve the molybdate in ammonia, add an excess of sulphuric acid, pass the warm solution through a column of zinc and titrate the reduced molybdic acid with standard potassium permanganate, the amount of permanganate required being a measure of the phosphorus present.

The impurities interfering in the procedures are silica and arsenic acid. The first may be eliminated by dehydration of the silicic acid in the solution and its removal as insoluble $SiO_2$ by filtration. Arsenic in small quantities does not interfere under certain conditions; in large quantities its removal is imperative.

### Preparation and Solution of the Sample

**Amount of the Sample Required.** — For accurate results it is advisable to take a fairly large sample, 5 to 10 grams, and when it has been dissolved, to dilute to a definite volume, 500 or 1000 cc. Aliquots of this solution are taken for analysis.

**Iron Ores, Phosphate Rock and Minerals.** — Five to 10 grams of the pulverized material placed in a 3 in. porcelain dish are digested for an hour with 50 to 100 cc. of concentrated hydrochloric acid (sp.gr. 1.19), the dish being covered by a clock-glass and placed on a steam bath. The acid is now diluted with half its volume of water and the solution filtered into a porcelain dish of sufficient capacity to hold the filtrate and washings. The residue is washed with dilute hydrochloric acid (1:1) until free of visible iron discoloration. The filtrate and washings are evaporated rapidly on a hot plate to small volume and then to dryness over the steam bath. Meanwhile the *insoluble residue* and filter are ignited in a 20 cc. platinum crucible

over a Meker burner or in a muffle furnace and the residue fused with ten times its weight of sodium carbonate. The fusion is removed by inserting a platinum wire into the molten mass, allowing to cool and then gently heating until the mass loosens from the crucible, when it may be removed on the wire. The cooled mass on the wire and that remaining in the crucible are dissolved in dilute hydrochloric acid, and the filtered solution added to the main solution. The combined solutions are evaporated to dryness, and heated gently to dehydrate the silica. The residue is taken up with a few cc. of hydrochloric acid, the solution diluted, filtered and the $SiO_2$ washed with dilute nitric acid solution. The combined filtrates are made up to 500 or 1000 cc. Aliquots of this solution are taken for analysis.

**Iron and Steel.** — Five to 10 grams of the drillings or filings are dissolved in an Erlenmeyer flask with 50 to 100 cc. of dilute nitric acid, 1:1, more acid being added if necessary. When dissolved, a strong solution of $KMnO_4$ is added until a pink color appears; on boiling brown manganese dioxide forms in the solution if a sufficient amount of permanganate has been added. This is dissolved by adding 2% sodium thiosulphate solution in just sufficient quantity to dissolve the precipitate. The solution is diluted to a convenient volume for analysis. Where a number of determinations are to be made, it is advisable to weigh the amount of sample desired for the determination and to precipitate the ammonium phosphomolybdate in the flask in which the drillings have been dissolved.

**Ores Containing Titanium.** — Titanium may be recognized by the red color produced by hydrogen peroxide, $H_2O_2$, added to the sulphuric acid extract; also by the reduction test with zinc, which causes a play of colors, the solution becoming colorless by the reduction of iron, then, in presence of titanium, pink, purple and finally blue. (Vanadium gives similar tests.) Solutions containing titanium frequently appear milky when the solution is diluted before filtering off the insoluble residue. Since titanium forms an insoluble compound with phosphoric acid and iron oxide the final residue, obtained by the method of solution for ores, phosphate rock and minerals, should be moistened with sulphuric acid and the silica expelled with hydrofluoric acid. The solution is evaporated to dryness and to $SO_2$ fumes, the residue fused with sodium carbonate and taken up with boiling water. $TiO_2$ remains insoluble, while $P_2O_5$ passes into the filtrate.

## GRAVIMETRIC METHODS FOR DETERMINATION OF PHOSPHORUS

### A. DIRECT WEIGHING OF THE AMMONIUM PHOSPHOMOLYBDATE PRECIPITATION OF AMMONIUM PHOSPHOMOLYBDATE

*Precipitation of ammonium phosphomolybdate is common to all subsequent methods for determination of phosphorus, and, as in case of preparation and solution of the sample, details of this procedure will not be repeated.*

**Reaction.**

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 = (NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O.$$

**Special Reagents Required.** — *Ammonium Molybdate.* — One hundred grams of pure molybdic acid are thoroughly mixed with 400 cc. of cold distilled water and 80 cc. of strong ammonia (sp.gr. 0.90) added. When the solution is complete it is poured slowly and with constant stirring into a mixture of 400 cc. of strong nitric acid (sp.gr. 1.42) and 600 cc. of distilled water. This order of procedure should be followed, as the nitric acid poured into the ammonium molybdate solution will cause the precipitation of a difficultly soluble oxide of molybdenum. 0.05 gram of microcosmic salt, dissolved in a little water, are added, the precipitate agitated, then allowed to settle for twenty-four hours and the clear solution decanted through a filter into a large reagent bottle. Sixty cc. of the reagent should be used for every 0.1 gram of $P_2O_5$ present in the solution analyzed.

**Potassium Permanganate.** — For oxidation purposes a two per cent solution filtered free of dioxide through asbestos is required.

**Amount of Sample Required for Analysis.** — If the material contains over 20% $P_2O_5$, 0.1 to 0.5 gram sample should be taken; if the product contains 5 to 20% $P_2O_5$, 0.1 to 0.5 gram should be taken; for a sample containing 0.5 to 5%, 2.5 to 1 gram sample is taken, and for $P_2O_5$ less than 0.5%, a 5 gram sample is taken.

**Precipitation.** — The free acid of the solution is nearly *neutralized* by *addition of ammonium hydroxide.* In analysis of phosphate rock or materials comparatively low in iron, it is advisable to add ammonium hydroxide in quantity sufficient to cause a slight permanent precipitate followed by just sufficient $HNO_3$ to dissolve the precipitate. In *iron and steel* analysis ammonium hydroxide is added until the precipitated iron hydroxide dissolves with difficulty and the solution becomes a deep amber color or cherry red. In analysis of *soluble phosphates*, litmus paper dropped into the solution indicates the neutral point. *Nitric acid* is added to the neutral or slightly acid solution, 5 cc. of acid for every 100 cc. of solution. A volume of 150 to 200 cc. of solution is the proper dilution for samples taken in

amounts above recommended. To the warm solution (not over 80° C.) *ammonium molybdate is added*, 60 cc. of the reagent being required for every 0.1 gram of $P_2O_5$ present. The solution is stirred, or shaken, if in a flask, until a cloudy precipitate of ammonium phosphomolybdate appears. It is then allowed to settle on the steam bath at a temperature of 40 to 60° C., for half an hour, then again agitated and allowed to settle in the cold for half an hour or longer. The filtrate should be tested with additional ammonium molybdate for phosphorus. The yellow precipitate is filtered and washed with 1% $HNO_3$ solution followed by a 1% solution of $KNO_3$, or $NH_4NO_3$ or $(NH_4)_2SO_4$ as the special case requires. Filtration through asbestos in a Gooch crucible is to be recommended. When a large number of determinations are to be made, as in case of iron and steel, filter paper is more convenient. After a final washing with water the precipitate, free from contaminating impurities, is dried for two hours in an oven at 110° C., then cooled in a desiccator and weighed. Weight of precipitate $\times$ 0.0165 = P, or $\times$ 0.03784 = $P_2O_5$.

Note. If this procedure is to be followed it will be convenient to take 1.65 grams sample, if the phosphorus content will allow. Each 0.01 gram of precipitate will then equal 1% P.

## B. DETERMINATION OF PHOSPHORUS AS MAGNESIUM PYROPHOSPHATE

**Magnesia Mixture.** — For precipitation of ammonium magnesium phosphate, 110 grams of magnesium chloride ($MgCl_2.6H_2O$) are dissolved in a small amount of water. To this are added 280 grams of ammonium chloride and 700 cc. of ammonia (sp.gr. 0.90); the solution is now diluted to 2000 cc. with distilled water. The solution is allowed to stand several hours and then filtered into a large bottle with glass stopper. Ten cc. of the solution should be used for every 0.1 gram of $P_2O_5$ present in the sample analyzed. As the reagent becomes old it will be necessary to filter off the silica that gradually accumulates from the reagent bottle.

**Procedure.** — The ammonium phosphomolybdate,[1] obtained as directed (under *A*), is filtered onto a rapid filtering filter paper and washed four or five times with dilute 1% $HNO_3$. The precipitate is now dissolved from the filter by a fine stream of hot ammonium hydroxide, 1:1, catching the solution in the beaker in which the precipitation was made. The solution and washings should be not over 100 to 150 cc. Hydrochloric acid is added to the cooled solution to neutralize the excess of ammonia, the yellow precipitate, that forms during the neutralization, dissolving with difficulty when sufficient

[1] Note. In absence of heavy metals whose phosphates are insoluble in ammonia the magnesia mixture may be added directly to the neutral solution containing the phosphate, without previous precipitation as molybdate.

acid has been added. To the cooled solution *cold magnesia mixture is added* drop by drop (2 drops per second) with constant stirring. Ten cc. of the reagent will precipitate 0.1 gram of $P_2O_5$. When the solution becomes cloudy the stirring is discontinued and the precipitate allowed to settle ten minutes. *Ammonium hydroxide is added* until the solution contains about one-fourth its original volume of strong ammonia (e.g. 25 cc. of $NH_4OH$, 90 to 100 cc. of solution). The solution is stirred during the addition and then allowed to settle for an hour or more. It is filtered preferably through a Gooch crucible (or through an ashless filter paper), and the precipitate washed with dilute ammonium hydroxide, 1 : 4, then placed in a porcelain crucible, a few drops of saturated solution of ammonium nitrate added and the precipitate heated over a low flame till decomposed (or until the paper chars). The lumps of residue are broken up with a platinum rod and again ignited over a Scimatco or Meker burner, the heat being gradually increased. If the heating is properly conducted, the resultant ash will be white or light gray, otherwise it will be dark. The addition of solid ammonium nitrate aids the oxidation in obstinate cases but there is danger of slight mechanical loss. The crucible is cooled in a desiccator and the residue weighed as magnesium pyrophosphate.

$$Mg_2P_2O_7 \times 0.2787 = P \quad \text{and} \quad Mg_2P_2O_7 \times 0.6379 = P_2O_5.$$

## VOLUMETRIC METHODS FOR THE DETERMINATION OF PHOSPHORUS

These volumetric procedures are especially applicable for determining small amounts of phosphorus such as are present in steel and in alloys.

### C. ALKALIMETRIC METHOD

The method is based on the acid character of ammonium phosphomolybdate, the following reaction taking place with an alkali hydroxide:

$$2(NH_4)_3.12MoO_3.PO_4 + 46NaOH + H_2O = 2(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 23H_2O$$

From the reaction 46 molecules of sodium hydroxide are equivalent to one molecule of $P_2O_5$, hence 1 cc. of a N/10 solution of sodium hydroxide neutralizes the yellow precipitate containing an equivalent of .000309 gram of $P_2O_5$.

**Solutions Required.** — *Nitric Acid for Dissolving:* Mix 1000 cc. of $HNO_3$, sp.gr. 1.42 and 1200 cc. of distilled water.

*Nitric Acid for Washing:* Mix 20 cc. of $HNO_3$, sp.gr. 1.42, and 1000 cc. of distilled water.

*Ammonium Molybdate:* Solution No. 1. Place in a beaker 100 g. of 85 per cent molybdic acid, mix it thoroughly with 240 cc. of distilled water, add 140 cc. of $NH_4OH$, sp.gr. 0.90, filter and add 60 cc. of $HNO_3$, sp.gr. 1.42.

Solution No. 2. Mix 400 cc. of $HNO_3$, sp.gr. 1.42, and 960 cc. of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly; then add 0.01 gram of ammonium phosphate dissolved in 10 cc. of distilled water and let stand at least 24 hours before using.

*Potassium Nitrate, 1 per cent:* Dissolve 10 g. of $KNO_3$ in 1000 cc. of distilled water.

*Phenolphthalein Indicator:* Dissolve 0.2 g. of phenolphthalein in 50 cc. of 95 per cent ethyl alcohol and 50 cc. of distilled water.

*Standard Sodium Hydroxide:* Dissolve 6.5 g. of purified NaOH in 1000 cc. of distilled water, add a slight excess of 1 per cent solution of barium hydroxide, let stand for 24 hours, decant the liquid, and standardize it against a steel of known phosphorus content as determined by the molybdate-magnesia method, so that 1 cc. will be equivalent to 0.01 per cent of phosphorus on the basis of a 2 g. sample (see notes).

Protect the solution from carbon dioxide with a soda-lime tube.

*Ferric Chloride:* Dissolve 100 g. of ferric chloride (phosphorus free) in 100 cc. of distilled water.

*Standard Nitric Acid:* Mix 10 cc. of $HNO_3$, sp.gr. 1.42, and 1000

cc. of distilled water. Titrate the solution against standardized NaOH, using phenolphthalein as indicator, and make it equivalent to the NaOH by adding distilled water.

### (*a*) Method for Copper Alloys

In a 400 cc. casserole dissolve 1 g. of copper alloy metal in 10 cc. of $HNO_3$, sp.gr. 1.42. Add 20 cc. of HCl, sp.gr. 1.20, and evaporate to dryness. Moisten with HCl, evaporate to dryness again, and bake to dull redness. Moisten with HCl again (add 3 cc. of ferric chloride solution unless iron is already present) and dilute to about 200 cc. with distilled water. Add $NH_4OH$, sp.gr. 0.90, until the basic salts of copper have dissolved and the solution has become a deep blue. Boil, allow to settle, and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with hot dilute HCl, dilute the solution to about 200 cc., add $NH_4OH$, sp.gr. 0.90, until the precipitate which forms at first dissolves rather slowly, and saturate with $H_2S$ gas. Filter off and reject the precipitate. Boil the filtrate to expel $H_2S$, and add $HNO_3$, sp.gr. 1.42, until the iron is oxidized. Add $NH_4OH$, sp.gr. 0.90, until the solution is alkaline. Boil and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with $HNO_3$ (sp.gr. 1.42) receiving the solution in a 350 cc. Erlenmeyer flask. Add $NH_4OH$, sp.gr. 0.90, until the iron is entirely precipitated, and then add $HNO_3$, sp.gr. 1.42, cautiously until the solution just becomes clear. Bring the solution to a temperature of about 80° C., and add 40 cc. of ammonium molybdate at room temperature. Allow to stand for one minute, shake or agitate for 3 minutes, and filter on a 9 cm. paper. Wash the precipitate three times with the 2 per cent $HNO_3$ solution to free it from iron, and continue the washing with the 1 per cent $KNO_3$ solution until the precipitate and flask are free from acid.

Transfer the paper and precipitate to a solution flask, add 20 cc. of distilled water, 5 drops of phenolphthalein solution as indicator, and an excess of standard NaOH solution. Insert a rubber stopper and shake vigorously until solution of the precipitate is complete. Wash off the stopper with distilled water and determine the excess of NaOH solution by titrating with standard $HNO_3$ solution. Each cubic centimeter of standard NaOH solution represents 0.01 per cent of phosphorus.

*Accuracy:* Duplicate determinations should check within 0.01 per cent of phosphorus.

Notes. The ammonium-molybdate solution should be kept in a cool place and should always be filtered before using.

All distilled water used in titrations should be freed from carbon dioxide by boiling or otherwise.

Bureau of Standards Standard Steel No. 19 (*a*) is recommended as a suitable steel of standardization of the NaOH solution.

### (*b*) Method for Steel

**Procedure.** — The ammonium phosphomolybdate, obtained according to directions already given on page 439, is filtered into a Gooch crucible containing asbestos, and washed once or twice with water containing 1% nitric acid, and then several times with a 1% neutral solution of potassium nitrate until the washings are free of acid, as indicated by testing with litmus paper. The asbestos mat containing the precipitate is transferred to a No. 4 beaker, 100 cc. of $CO_2$ free water added, followed by about 20 cc. of N/10 NaOH measured from a burette. The crucible is rinsed out with 5 to 10 cc. of N/10 NaOH, the exact amount being noted and then with water, adding the rinsings to the main solution. Phenolphthalein indicator is added, and the excess of caustic titrated with N/10 $HNO_3$. The total NaOH added minus the acid titration equals the cc. of the caustic required to react with the yellow precipitate.

One cc. of N/10 NaOH = 0.000136 gram of P and = 0.000309 gram of $P_2O_5$.

The exact factor should be determined as directed under Reagents.

## D. ZINC REDUCTION AND TITRATION WITH POTASSIUM PERMANGANATE

**Permanganate. — Ferric-Alum Method.** — This method is based on the assumption that ammonium phosphomolybdate, $(NH_4)_3.12MoO_3.PO_4$, is reduced, in acid solution, by zinc, the molybdic acid, $MoO_3$, forming the lower oxide $Mo_2O_3$, in which form it reacts with ferric iron in the receiving flask, reducing a corresponding equivalent of ferric salt to ferrous condition, being itself oxidized to $MoO_3$. When the ferric solution is not placed in the receiving flask a slight oxidation takes place, the oxide $Mo_{24}O_{37}$, apparently being formed.

### Special Apparatus Required

**Jones' Reductor.** — Details of the reductor are given under the determination of iron by the permanganate method, also under the Volumetric Determination of Molybdenum, pages 319, 393.

**Solutions Required.** —

*Dilute Ammonia:* Mix 100 cc. of $NH_4OH$, sp.gr. 0.90, and 900 cc. of distilled water.

*Dilute Hydrochloric Acid:* Mix 500 cc. of HCl, sp.gr. 1.20, and 500 cc. of distilled water.

*Dilute Sulphuric Acid for Dissolving:* Mix 200 cc. of $H_2SO_4$, sp.gr. 1.84, and 800 cc. of distilled water.

*Dilute Sulphuric Acid for Reductor:* Mix 500 cc. of $H_2SO_4$, sp.gr. 1.84, and 500 cc. of distilled water.

*Ammonium Molybdate:* Solution No. 1. Place in a beaker 100 g. of 85 per cent molybdic acid, mix it thoroughly with 240 cc. of distilled water, add 140 cc. of $NH_4OH$, sp.gr. 0.90, filter and add 60 cc. of $HNO_3$, sp.gr. 1.42.

Solution No. 2. Mix 400 cc. of $HNO_3$, sp.gr. 1.42, and 960 cc. of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly, then add 0.1 g. of ammonium phosphate dissolved in 10 cc. of distilled water, and let stand at least 24 hours before using.

*Acid Ammonium Sulphate:* Mix 25 cc. of $H_2SO_4$, sp.gr. 1.84, and 1000 cc. of distilled water, and then add 15 cc. of $NH_4OH$, sp.gr. 0.90.

*Ferric Alum:* Dissolve 200 g. of ferric ammonium sulphate crystals in 1950 cc. of distilled water. Add 50 cc. of $H_2SO_4$, sp.gr. 1.84, and 80 cc. of phosphoric acid, 85 per cent.

*Potassium Permanganate:* Dissolve from 3.0 to 3.2 g. of $KMnO_4$ in 1000 cc. of distilled water. Allow the solution to stand for about one week, and then filter it through an asbestos filter. Standardize by using about 0.200 g. portions of pure sodium oxalate.

**Standard for Phosphorus in Steel.** — The exact value of the permanganate solution may be accurately and rapidly determined in terms of phosphorus by standardizing against a sample of standard steel containing a known amount of phosphorus, the ultimate standard being steel drillings furnished by the Bureau of Standards. The drillings are dissolved in nitric acid, oxidized with $KMnO_4$, the excess of the reagent being destroyed by thiosulphate solution. Ammonia is added until the solution becomes a deep amber color. The phosphorus is precipitated as ammonium phosphomolybdate. The following procedure is the same as is given in the volumetric method following: The permanganate titration of the reduced molybdic acid divided into the amount of phosphorus known to be present in the solution will give the value of the permanganate in terms of phosphorus.

$$\frac{\text{Wt. of P in sample}}{\text{cc. } KMnO_4 \text{ required}} = \text{amount of P per cc. of } KMnO_4.$$

**Method.** — In a 400 cc. casserole dissolve 1 g. of the metal in 10 cc. of $HNO_3$, sp.gr. 1.42. Add 20 cc. of HCl, sp.gr. 1.20, and evaporate to dryness. Moisten with HCl, evaporate to dryness again, and bake to dull redness. Moisten with HCl again, and dilute to about 200 cc. with distilled water and filter if cloudy. To the solution add $NH_4OH$, sp.gr. 0.90, until the iron is entirely precipitated, and then add $HNO_3$, sp.gr. 1.42, cautiously until the solution just becomes clear, the solution having an amber color. Bring the solution to a temperature of about 80° C., and add 40 cc. of ammonium molybdate at room temperature. Allow to stand for one minute, shake or agitate for 3 minutes, filter on a 9 cm. paper, and wash very thoroughly (about 25 times) with acid ammonium sulphate. Dissolve the precipitate on the paper using 50 cc. of dilute ammonia. Add 10 cc. of $H_2SO_4$, sp.gr. 1.84, and immediately pass the solution through a Jones reductor, which has the reductor tube prolonged and reaching nearly to the bottom of the flask, dipping into 50 cc. of ferric-alum solution. Wash through the reductor with 150 cc. of distilled water, and follow with an additional 100 cc. of distilled water. Titrate with standard $KMnO_4$.

By this method the molybdenum in passing through the reductor is reduced entirely to the form $Mo_2O_3$, and is oxidized by the ferric alum to the form $MoO_3$, an equivalent amount of iron being reduced to the ferrous condition. As the yellow precipitate contains one atom of phosphorus to each twelve molecules of $MoO_3$, and as three atoms of oxygen oxidize two of molybdenum, eighteen oxygens or thirty-six irons are equivalent to one phosphorus. Therefore, the iron value of the permanganate multiplied by the factor P/36 Fe (or 0.01540) gives the value of the permanganate in terms of phosphorus.

*Accuracy:* Duplicate determinations should check within 0.01 per cent of phosphorus.

Notes. The ammonium-molybdate solution should be kept in a cool place and should always be filtered before using.

A blank determination should be made on corresponding amounts of acid and water, passing through the reductor into the usual amount of ferric-alum solution in the flask.

A small quantity of liquid should always be left in the reductor funnel, and air should never be allowed to enter the reductor.

Description of the Jones reductor is given on page 319, Volume I, "Standard Methods of Chemical Analysis," by W. W. Scott.

NOTES. During the titration, the solution changes in color to a brown, a pinkish yellow and finally to pink.

*Calculation.* CASE 1. If ferric sluphate is in the receiver ($6Mo_2O_3 + 18\ O = 12MoO_3$ in the molecule containing 1 P); 18 O are equivalent to 36 H, hence N/10 P according to this reaction equals at.wt. P divided by $(36 \times 1000)$ = P for 1 cc. of N/10 $KMnO_4$ = .0000862 g. P.

CASE 2. No ferric salt in receiver. $Mo_{24}O_{37} + 35\ O = 24MoO_3 + 2P.(35\ O = 70\ H)$. Dividing by 2 we get at.wt. P divided by $(35 \times 1000)$ = P for 1 cc. of N/10 $KMnO_4$ = .0000887.

## VOLUMETRIC DETERMINATION OF FREE PHOSPHORIC ACID

Phosphoric acid may be titrated directly by means of standard sodium or potassium hydroxide. The choice of the indicator is important as may be seen by the following reactions:

$H_3PO_4 + NaOH = H_2O + NaH_2PO_4$ (neutral to methyl orange, acid to phenolphthalein),

$H_3PO_4 + 2NaOH = 2H_2O + Na_2HPO_4$ (neutral to phenolphthalein, and alkaline to methyl orange).

The slight dissociation of $Na_2HPO_4$ causing an alkaline reaction to phenolphthalein prevents the end-point being sharp. This dissociation may be repressed by titrating in a cold concentrated solution containing sodium chloride. The first reaction with methyl orange indicator is more satisfactory. By the electrometric method J. S. Coye has shown that the end-point of phenolphthalein is the full color of the alkaline salt, not a faint pink.

## PLATINUM

**Pt, at.wt. 195.2; sp.gr. 21.48; m.p. 1755° C.; oxides PtO, $PtO_2$**

### OCCURRENCE

Platinum may be present under the following conditions:

1. Native grains usually accompanied by the other so-called platinum metals, iridium, palladium, ruthenium, rhodium, osmium, and gold and silver (alloyed with one or more of the allied metals).

Ore concentrates containing the native grains as above with the base metals, iron, copper, chromium, titanium, etc. The associated minerals high in specific gravity in the gravels may be expected to appear with the platinum nuggets, such as chromite, magnetite, garnet, zircon, rutile, small diamonds, topaz, quartz, cassiterite, pyrite, epidote, and serpentine; with gold in syenite; ores of lead and silver.

2. Scrap platinum containing, oftentimes, palladium, iridium, gold, silver and iron.

3. Small amounts of platinum in the presence of large amounts of iron, silicon, carbon, magnesium: platinum residues, nickel and platinum contacts, photography paper, jewelers' filings and trimmings, dental and jewelers' sweepings and asbestos from "contact material," etc.

4. Platinum alloyed with silver, gold, tungsten, nickel, copper, lead, etc.

5. Platinum solutions and salts.

**Minerals.** — Platinum is found native in nature, generally alloyed with the so-called platinum metals, iridium, palladium, ruthenium, rhodium and osmium. Iron is invariably present sometimes to the extent of 15–20%. The impure metal occurs in small grains or nuggets in alluvial sands and in placer deposits. The most important platinum placers are in the Ural mountains.

*Sperrylite*, $PtAs_2$; *Platin-Iridium*, alloy of Pt, Pd, Rh, Os and Ir. *Palladium* alloyed with Pt and Ir: Iridosmine, Ir, Os, Rh, Pt etc.

### DETECTION

**Platinum** is a gray, lustrous, soft and malleable metal. It is not altered by ignition in the air, but fuses in the oxy-hydrogen flame. It does not dissolve in any of the single acids, but a fusion with acid potassium sulphate attacks the metal slightly. The action of chlorine in general, and nitro-hydrochloric acid (aqua regia), the main solvent, converts the metal to hydrochlorplatinic acid, $H_2PtCl_6$, which forms many double salts, or platinichlorides. If platinic chloride is gently heated it breaks up into platinous chloride, $PtCl_2$, and chlorine.

If, however, the platinum is alloyed with silver, it dissolves in nitric acid to a yellow liquid, provided sufficient silver is present in the alloy.

The oxides can be formed by carefully igniting the corresponding hydroxides. These are very unstable, decomposing into metal and oxygen by gentle ignition.

The chlorides are the most important compounds of platinum. Two complex acids are formed with hydrochloric acid when the metal is dissolved in aqua regia.

$PtCl_4 + 2HCl = H_2PtCl_6$ (hydrochlorplatinic acid), orange-red crystals.

$PtCl_2 + 2HCl = H_2PtCl_4$ (hydrochlorplatinous acid), only known in solution.

An aqueous solution of the former is yellowish-orange, while an aqueous solution of the latter is dark brown, the former being by far the more important.

**Potassium iodide** precipitates platinic iodide, but it dissolves quite readily, giving a pink to a dark blood-red liquid, depending on the concentration of the solution. Nitric acid should be absent. The color is destroyed by heat, also by hydrogen sulphide, sodium thiosulphate and sulphite, sulphurous acid, mercuric chloride and certain other reducing reagents.

**Hydrogen sulphide** precipitates black platinic disulphide, $PtS_2$, with the other elements of the hydrogen sulphide group. The solution should be warm, as precipitation takes place more quickly. It is difficultly soluble in ammonium sulphide. It will be found in the extract with the arsenic, antimony, tin, gold, molybdenum, etc., and is precipitated with these elements upon addition of hydrochloric acid. Platinic sulphide is soluble in aqua regia. Addition of 75% $MgCl_2$ solution prevents formation of colloidal $PtS_2$.

**Ammonium chloride** added to a concentrated solution of platinic chloride precipitates yellow $(NH_4)_2PtCl_6$, which is slightly soluble in water, but insoluble in dilute ammonium chloride solution and alcohol.

**Potassium chloride** precipitates yellow $K_2PtCl_6$, which is difficultly soluble in water, but insoluble in 75% alcohol.

**Ferrous sulphate** on boiling precipitates metallic platinum from a neutral solution. Neutralize with $Na_2CO_3$. Free mineral acids (except dilute $H_2SO_4$) prevent the precipitation (difference from gold).

**Stannous chloride** does not reduce platinic chloride to metal, but reduces hydrochlorplatinic acid to hydrochlorplatinous acid.

$$H_2PtCl_6 + SnCl_2 = H_2PtCl_4 + SnCl_4.$$

**Oxalic acid** does not precipitate platinum (difference from gold).

**Sodium hydroxide with glycerine** reduces hydrochlorplatinic acid on warming to black metallic powder.

**Formic acid** precipitates from neutral boiling solution all the platinum as a black metallic powder.

**Thallium protoxide** precipitates from the platinous chloride solution a pale yellow salt, thallium platinochloride. When the salt is heated to redness it leaves an alloy of thallium and platinum.

**Rubidium, caesium and thallium chlorides** yield similar insoluble salts with platinic chloride.

**Sodium hydroxide** added to platinic chloride and then supersaturated with acetic acid produces a reddish-brown precipitate of platinic hydroxide $Pt(OH)_4$. This dissolves in acids readily, except acetic acid.

**Metallic zinc, magnesium, iron, aluminum and copper** are the most important metals that precipitate metallic platinum.

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

The best solvent for platinum is aqua regia. The metal is also acted upon by fusion with the fixed alkalies — sodium or potassium hydroxide and sodium peroxide or potassium or sodium nitrate; also by chlorates in the presence of HCl. Platinum, when highly heated, alloys with other metals, such as lead, tin, bismuth, antimony, silver, gold, copper, etc. The element dissolves in nitric acid when alloyed with silver. This gives a method for the determination of gold in the presence of silver and platinum alloy.

All salts of platinum are soluble in water. The less soluble salts are the chloroplatinates of potassium, ammonium, rubidium, and caesium. Heat increases the solubility while the presence of alcohol decreases the solubility.

**Ores.** — When the free grains of platinum, gold and osmiridium are desired the following method is recommended: Five to 10 grams of the ore are taken from a well-mixed pulverized sample and placed in a large platinum dish that has been weighed. Twenty-five to 50 cc. of strong hydrofluoric acid together with 5 to 10 cc. of concentrated sulphuric acid is mixed with the ore in the dish and evaporated on the water bath, when $SiF_4$ and the excess of HF are expelled. The material is gently heated until $SO_3$ fumes are given off. This is repeated with HF if necessary. The material is washed into a casserole with about 200 cc. of hot water and digested over a water bath for fifteen or twenty minutes, and is then washed by decantation, several times pouring the supernatant liquor through a filter to save any floating material that might be washed out. The filter is cautiously burned and the residue is added to the unattacked material. This is transferred from the dish to a beaker or a porcelain dish and treated with aqua regia. The platinum and a small amount of iridium that dissolves with the platinum on account of its being alloyed can be precipitated with ammonium chloride. The remaining residue in the dish will be a small amount of sand and osmiridium. The silica is driven off with HF as described above and the bright grains weighed as osmiridium, or the sand and osmiridium are run down in a scorifier with lead, and the lead dissolved in dilute nitric acid, leaving the osmiridium grains free from sand.

**Platinum Scrap.** — One-half gram to a gram is dissolved in aqua regia and evaporated with HCl to get rid of the $HNO_3$.

If the platinum is alloyed with a large amount of copper, silver, lead and other impurities, a sample of 1 to 5 grams is dissolved in 15 to 25 cc. of $HNO_3$, whereby the copper, silver, lead and other impurities alloyed with the platinum as well as a large amount of platinum will dissolve. The residue after washing will be platinum and gold. These are dissolved in aqua regia as described above and the

platinum precipitated with ammonium chloride. The platinum is recovered from the nitric acid solution and added to the aqua regia solution and the whole is evaporated to get rid of the $HNO_3$.

**Small Amounts of Platinum in the Presence of Large Amounts of Iron; Iron Scale, $Fe_2O_3$; Sulphate of Iron, Sulphate of Magnesium, Silica, etc.** — The material is carefully weighed and the coarse scales are separated from the finer material containing the platinum by passing the fines through a 20-in. mesh or finer wire sieve. The coarse scale seldom contains platinum, but it is advisable to quarter this down to 1 kilogram or a fairly good-sized sample and test for platinum on a portion of the ground sample. This can be tested by a wet or a fire assay. The fines are quartered down to about 1 kilogram and ground to pass a 60 to 80 in. mesh sieve. One hundred to 500 grams of the material are taken for analysis. This is placed in one or more casseroles, depending on the amount taken. Each 100-gram portion is extracted by digestion on the steam bath with about 300 to 400 cc. of 10% $H_2SO_4$. The iron, magnesium, etc., soluble in $H_2SO_4$ will go into solution, leaving the platinum with the insoluble residue. Filter (a Buchner funnel may be necessary) and wash the residue with water. Test the filtrate for platinum and if any is present precipitate with zinc as described below.

After the filter is ignited in a large platinum dish, the residue is moistened with $H_2SO_4$, and HF is added completely covering the material. The solution is evaporated on the water bath until $SO_3$ fumes are given off. If necessary, the treatment is repeated with $H_2SO_4$ and HF until all the silica is driven off as $SiF_4$. The residue is transferred to a casserole and digested with aqua regia according to directions given under Ores and Platinum Scrap. It is sometimes very difficult to precipitate all of the platinum in the presence of a large amount of iron, magnesium, etc., not having the solution concentrated enough for the platinum. It is advisable to reduce the platinum by iron or zinc, filter, wash with water and redissolve the black metallic platinum in aqua regia. The $HNO_3$ is expelled by evaporation, adding concentrated HCl from time to time. Finally the platinum is precipitated with ammonium chloride.

## Separations

A careful review of the paragraph on Detection will be very helpful oftentimes in making separations from other metals and substances.

**Separation of Platinum from Gold.** — The platinum is precipitated first with ammonium chloride, as $(NH_4)_2PtCl_6$. After the precipitate has settled it is filtered and washed free from gold with 20% ammonium chloride solution and alcohol. The gold is precipitated as metallic gold by a concentrated solution of ferrous sulphate or iron protochloride.

Oxalic acid precipitates the gold, leaving the platinum in solution. The oxalic acid is added and the solution heated until the gold is entirely precipitated. The precipitate of metallic gold free from platinum is filtered off and washed. The filtrate is evaporated as far as possible without crystallizing, and the platinum is precipitated with ammonium chloride as $(NH_4)_2PtCl_6$, or it may be reduced with zinc and then dissolved in aqua regia and treated as described above.

**Separation of Platinum from Iridium.** — The platinum and the iridium are precipitated by iron or zinc, and the black residue is washed free from impurities and the platinum is dissolved in dilute aqua regia with gentle heating, leaving the iridium as metallic iridium. The platinum solution is evaporated as described above as precipitated with $NH_4Cl$ as $(NH_4)_2PtCl_6$.

If the platinum and iridium are precipitated together, the salt is filtered and washed with ammonium chloride solution and finally ignited. The sponge is redissolved and evaporated as above to expel the $HNO_3$. The platinum and the iridium are precipitated with NaOH, which brings down the platinum and iridium as $Pt(OH)_4$ and $Ir(OH)_4$. The mixture is boiled with alcohol, which reduces the $Ir(OH)_4$ to $Ir(OH)_3$, but does not affect the $Pt(OH)_4$. The hydroxides are dissolved in HCl, forming $PtCl_4$ and $IrCl_3$ in solution, and the platinum is precipitated with $NH_4Cl$ free from iridium.

**Separation of Platinum from Palladium.** — The platinum and the palladium are reduced with zinc and the black residue treated with $HNO_3$. The palladium goes into solution, leaving the platinum as a black metallic residue.

The black residue of platinum and palladium can be dissolved in aqua regia and the solution evaporated with additions of HCl to get rid of the nitric acid. The platinum is precipitated with $NH_4Cl$ and filtered. The filter is washed free from palladium.

**Separation of Platinum from Ruthenium.** — From the chloride of platinum and ruthenium the metals are precipitated with ammonium or potassium chloride and filtered. The filter is washed with dilute ammonium chloride solution or dilute potassium chloride solution and alcohol until free from ruthenium. If a large quantity is handled it may be necessary to ignite to platinum sponge, dissolve in aqua regia, expel the $HNO_3$ as described above, and reprecipitate with $NH_4Cl$, filter and wash free from ruthenium.

**Separation of Platinum from Rhodium.** — The rhodium salt, like the ruthenium salt, is soluble and can be washed from the platinum salt, $(NH_4)_2PtCl_6$, as under Separation of Pt from Ru.

**Separation of Platinum from Osmium.** — Both metals are reduced with zinc as a fine black powder. The metallic residue is washed and carefully ignited at a high temperature under a hood, as the fumes are poisonous and disagreeable like chlorine. The osmium will be converted into $OsO_2$ and $OsO_4$, which are very volatile. The residue is dissolved in aqua regia and the platinum is precipitated with $NH_4Cl$.

## GRAVIMETRIC METHODS FOR THE DETERMINATION OF PLATINUM

### A. WEIGHING AS METALLIC PLATINUM

1. When the platinum contains only a small amount of impurities a sample of 0.1 gram or more is taken and dissolved in aqua regia. The solution is gently heated until all is dissolved, adding another portion of aqua regia if necessary. The solution is evaporated, adding HCl from time to time in order to expel the $HNO_3$. After filtering, the solution is evaporated again and platinum precipitated with ammonium chloride. After stirring, the precipitate, $(NH_4)_2PtCl_6$, is allowed to settle, overnight if convenient, then filtered, washed with alcohol or ammonium chloride solution and alcohol, ignited to metal which will be in the form of metallic sponge, cooled in a desiccator and weighed as metallic platinum.

$$\frac{\text{Wt. of Pt found}}{\text{Wt. of sample taken}} \times 100 = \text{per cent of Pt in the material.}$$

2. When the platinum solution contains a large amount of impurities, as iron, nickel, magnesium, etc., it is advisable to reduce the platinum to black metallic platinum with zinc, iron or magnesium as follows: The solution is made acid (2 to 5% free HCl) by adding HCl. The Zn, Fe or Mg is added in small quantities at a time until the solution becomes colorless or until the platinum is completely precipitated.[1] After action has ceased the platinum black metal is filtered on an ashless filter paper and washed with warm dilute HCl to remove any excess Zn, Fe, or Mg that might be present. The filter and its contents are carefully ignited and afterwards dissolved in aqua regia and treated as directed under **A**, 1.

3. If none of the other Hydrogen Sulphide Group metals are present the platinum can be precipitated by hydrogen sulphide, filtered, washed with hot water and ignited to metal. If impurities are present in the sulphide, it is dissolved in aqua regia and procedure **A**, 1 followed.

[1] If iron and lead are suspected, the platinum residue is washed with 10% solution of ammonium chloride and then with 10% solution of ammonium acetate and finally with 80% alcohol.

### B. WEIGHING AS A SALT

1. The procedure is the same as under **A**. The $(NH_4)_2PtCl_6$ precipitate is washed on a weighed Gooch crucible with alcohol. The crucible and contents are dried at a temperature below 100°C., cooled in a desiccator and weighed as $(NH_4)_2PtCl_6$.

$$\text{Wt. of } (NH_4)_2PtCl_6 \text{ found} \times \frac{\text{Mol. wt. of Pt}}{\text{Mol. wt. of } (NH_4)_2PtCl_6} \times \frac{100}{\text{Wt. of sample}} = \text{per cent of Pt in material.}$$

Factor $(NH_4)_2PtCl_6$ to Pt = 0.4393.

2. After proceeding as described under **A**, the platinum is precipitated with potassium chloride as $K_2PtCl_6$, transferred to a weighed Gooch crucible and washed well with alcohol, then dried below 100°C., cooled in a desiccator and weighed as $K_2PtCl_6$.

$$\text{Wt. of } K_2PtCl_6 \text{ found} \times \frac{\text{Mol. wt. of Pt}}{\text{Mol. wt. of } K_2PtCl_6} \times \frac{100}{\text{Wt. of sample}} = \text{per cent of Pt in material.}$$

Factor $K_2PtCl_6$ to Pt = 0.4013.

### C. DETERMINATION OF PLATINUM BY ELECTRO-ANALYSIS

When platinum solutions are acidulated with sulphuric acid and acted upon by a feeble current they give up the metal as a bright deposit upon the electrode. If platinum is used as the electrode, first coat it with a layer of copper and deposit the platinum upon the copper. Wash with water and alcohol and after drying weigh.

Wt. of electrode + Cu + Pt − Wt. of electrode + Cu = Wt. of Pt.

$$\frac{\text{Wt. of Pt}}{\text{Wt. of sample taken}} \times 100 = \text{per cent of Pt in material.}$$

Dr. E. F. Smith, in his work on "Electro-Analysis" recommends that the $K_2PtCl_6$ be dissolved in water and slightly acidulated with $H_2SO_4$ (2 or 3% by vol.) and after heating to about 60 to 65° C and electrolyzing with $N.D._{100} = .05$ ampere and 1.2 volts, the platinum will be completely precipitated in from four to five hours in a perfectly adherent form. A rotating anode will precipitate the platinum much quicker.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Assay Methods of Platinum Ores, etc.

Take from 10 to 30 grams of the material and place in a $2\frac{1}{2}$- or 3 in. scorifier with about 20 to 30 grams of test lead and cover with litharge. Fuse in a muffle for a half hour. When cool clean the lead button thoroughly and dissolve the lead with dilute nitric acid (1 : 5). When the lead is dissolved, filter, and wash the residue with hot water till free from lead. Dry the filter and transfer the bulk of the residue to a small glass beaker. Burn the filter, and add the ash to the main residue. This is treated with dilute aqua regia to remove any gold, platinum, etc., that may be present. Filter and wash thoroughly with hot water and ignite at a low temperature for a short time only, as osmium will volatilize. Weigh as osmiridium. (See Ir and Os.)

Take another portion of 10 to 30 grams of the material and treat with aqua regia two or three times. This will bring the platinum and the alloys (except osmiridium) into solution. After filtering make up the volume to 500 to 1000 cc., depending on the amount of platinum present. Take two or three portions of 25 to 50 cc. of the solution and evaporate nearly to dryness with additions of HCl to get rid of the $HNO_3$. Take up with a small amount of water and add ammonium chloride. Digest on the water bath and let cool overnight if convenient. Filter on an ashless filter and wash with dilute ammonium chloride solution and alcohol. Ignite cautiously and weigh as platinum and iridium sponge. For the determination of iridium see under Iridium.

The filtrate from the platinum precipitation is treated with ferrous sulphate to precipitate the gold. Digest and filter out the gold. Ignite and alloy with silver and part for gold.

In the filtrate from the gold precipitation the palladium and rhodium are treated with zinc and HCl until the solution is colorless. Filter, wash well with hot water and dilute HCl.

Ignite, reduce in hydrogen, cool and weigh as Pd and Rh. Treat with $HNO_3$. Filter, wash well, ignite and reduce in hydrogen, cool and weigh as metallic rhodium. The difference is palladium. See alternate method described under palladium.

### Determination of Platinum and Palladium in Refined Silver

Weigh out a 1000 gram sample and dissolve it with dilute nitric acid. Filter off the gold and any undissolved platinum, and then separate the gold from the platinum as described under "Gold Bar," and add the solution to the main filtrate. Dilute the filtrate from the gold residue, so that there will be 10 grams of silver per liter of solution, and then add a slight excess of hydrochloric acid to pre-

cipitate all the silver. Stir well and let it settle. Decant the clear solution and wash the precipitate on a Buchner funnel with cold water. Evaporate the filtrate to a small volume. Now mix the silver chloride with about ten times its weight of soda ash (which contains a small amount of corn starch) and dry. Place the mass in 30-gram crucibles, and fuse for about 30 minutes. Pour in molds. When cool, hammer off excess of slag, and finally boil with hydrochloric acid to clean the silver buttons. Then dissolve with dilute nitric acid and precipitate silver as silver chloride, separating it from platinum. Another silver chloride precipitation will be necessary to separate all platinum and palladium from the silver.

Combine all filtrates and evaporate to dryness on steam plate. Take up with a few cc. of hydrochloric acid and water, filter off the silver chloride and wash with cold water. This small amount of silver chloride carries down considerable platinum and palladium. Therefore place the filter paper with the silver chloride in a 3 inch scorifier, dry, add 40 grams of test lead and a pinch of borax and scorify. Then cupel the lead button. Dissolve the silver buttons with dilute nitric acid and reprecipitate silver with hydrochloric acid. Finally when the pure white color of the silver chloride, indicates that it is free from platinum and palladium, evaporate the filtrate to dryness on steam plate. Take up with 16 cc. of hydrochloric acid and 4 cc. of water. Boil for a minute, filter, and precipitate platinum and palladium. See method in refined gold.

**Copper Anode Slimes.** — Take a 1000 gram sample. Weigh out 3 gram portions into 3 inch scorifiers and mix each with 40 grams of test lead and a pinch of borax and litharge. Scorify and cupel. Dissolve silver buttons with dilute nitric acid, and proceed as described above.

### Determination of Platinum and Palladium in Refined Gold [1]

The sample may be in the shape of drillings, but from a bar it is easier to roll the gold into a thin ribbon.

Fifty grams [2] of gold sample is sufficient for gold which has been parted with sulphuric and nitric acids.

Dissolve sample in a 1500 cc. beaker with 50 cc. of nitric acid (1.42) and 150 cc. of hydrochloric acid (1.19) using no water. Heating is not necessary. After complete solution of the sample, evaporate solution to a syrup of about 40 cc. volume, taking care not to evaporate too far, otherwise, some gold will become reduced and separate out; add 100 cc. of hydrochloric acid and re-evaporate the solution to syrup, repeating this operation four times in order to remove all nitric acid.

[1] Contributed by S. Skowronski, Chief Chemist, Raritan Copper Works, Perth Amboy, N. J.

[2] For gold which has been electrolytically refined by the Wohwill process, 100 grams of gold should be taken as a sample doubling the quantity of acid necessary for the solution.

After the last evaporation, dilute with hot water, boil, add about 50 cc. of hydrochloric acid (1.19) to clear up solution: volume of solution should be about 500 cc.

To the boiling solution[1] gradually add a mixture of 50 grams of ammonium oxalate and 50 grams of oxalic acid, which should precipitate all the gold, but should there be any doubt add more of the mixture of the salts. Dilute the solution to about 1000 cc. in volume and allow to settle in a warm place overnight.

Filter off the gold, washing by decantation into a 1500 cc. beaker. For extreme accuracy, this gold may be redissolved, re-evaporated and reprecipitated, this time with sulphur dioxide gas. This is more of a precautionary measure, for as a rule, no platinum or palladium will be found with the gold.

To the solution from the gold add 5 grams of 30 mesh C.P. zinc. This precipitates any gold left in the solution along with the silver, platinum, palladium, tellurium, copper, etc.

Filter as soon as precipitation is complete and wash by decantation keeping as much of the precipitate in the beaker as possible. Ignite filter paper and transfer residue and precipitate to a 250 cc. beaker, dissolve in 10 cc. of aqua regia and after complete solution, add 5 cc. sulphuric acid (1.84), evaporate to fumes of $SO_3$ and fume well,[2] cool, dilute to 100 cc., bring solution to boiling and add 1 drop of hydrochloric acid to precipitate the silver, filter in a 400 cc. beaker, dilute filtrate to 200 cc. volume, add 5 cc. of hydrochloric acid (1.19), and precipitate palladium with .5 gram of di-methyl glyoxime dissolved in 50 cc. of boiling water.[3]

Palladium di-methyl glyoxime, canary yellow in color, which possesses the same physical characteristics as the corresponding nickel salt, at once separates out. Allow to settle in a warm place for about five minutes. Filter in a Gooch crucible, wash with hot water, dry at 110° C. and weigh. Factor .3168.

To the filtrate from the palladium add 2 grams of 30 mesh C.P. zinc, which precipitates the platinum. Filter. Ignite precipitate and dissolve in aqua regia. Remove nitric acid by three evaporations

[1] Sulphur dioxide gas is not recommended for the precipitation of gold, as gold bullions contain a trace of tellurium, and in the presence of tellurium, palladium is precipitated as a telluride by sulphur dioxide gas. The gold precipitated with oxalic acid is free from palladium telluride and therefore may be reprecipitated with sulphur dioxide gas if a reprecipitation is thought necessary.

[2] The platinum and palladium after solution in aqua regia, and addition of sulphuric acid, should be well fumed, in order to reduce any gold remaining in the solution to the metallic condition, it is very essential that all the gold be removed at this stage, otherwise it is liable to contaminate the palladium di-methyl glyoxime.

[3] Palladium is best precipitated with di-methyl glyoxime in a 3–5% acid solution; gold if present will be reduced to the metallic condition and should be removed beforehand. Alcohol is not recommended as the solvent for the di-methyl glyoxime, as it slows up the precipitation of the palladium. A hot water solution works quicker, and should be filtered to remove insoluble matter before addition to the palladium solution.

with hydrochloric acid (1.19), taking care not to evaporate solution to dryness.[1] After the last evaporation, take up with not more than 10 cc. of water, and a few drops of hydrochloric acid. If necessary, filter, keeping volume at 10 cc. Add 2 grams of ammonium chloride, stir well, add 10 cc. of alcohol, and let stand one hour with an occasional stirring.

Filter off ammonium chlor-platinate in small Gooch crucible and ignite to platinum in the usual manner.[2]

[1] Any solutions containing platinum should never be evaporated to dryness, as platinum is easily reduced in baking to the "platinous" condition which is not precipitated with ammonium chloride.

[2] The author is indebted to Mr. R. E. Hickman, chief chemist, T. Bishop and Co. Platinum Works, and Dr. S. Skowronski, chief chemist, Raritan Copper Works, for material appearing in this chapter.

# POTASSIUM, SODIUM AND OTHER ALKALIES

The estimation of potassium and sodium is required in the analysis of rocks, clays, soils, ashes of plants, waters, brines, saline deposits, salts of the alkalies, many technical products, and in other cases. The determination of potassium is of special importance in the analysis of fertilizers. The estimation of lithium is desired in the analysis of lithium minerals, frequently in mineral waters, occasionally in rocks, and in certain other special cases. The estimation of rubidium and caesium is seldom required.

## POTASSIUM

**Potassium, K, at.wt. 39.10; sp.gr. 0.875; m.p. 62.5°; b.p. 757.5° C.; oxides $K_2O$, $K_2O_4$.**

### OCCURRENCE

Potassium is found in nature only in the combined state. The chloride and the sulphate occur in sea water. Large deposits of potassium chloride and sulphate are found generally above rock salt in Galicia and North Germany, notably in Strassfurt. Layers of these deposits are found twenty to thirty feet in thickness.

Potassium occurs in the plant and animal kingdoms. It is a necessary constituent in soils for plant growth and hence is frequently applied to soils in form of fertilizers.

**Minerals.** — Carnallite, $KCl.MgCl_2.6H_2O$; kainite, $MgSO_4.KCl.3H_2O$; sylvite, KCl; Nitre, potassium nitrate "saltpeter," $KNO_3$.

### Detection of Potassium

For the detection of potassium in insoluble compounds, bring the sample into solution by one of the methods given under Preparation and Solution of Sample. In other cases, prepare a strong solution of the material to be tested. Where only very small amounts of potassium are present, remove all the constituents from the solution except the chlorides of magnesium and the alkalies as directed under Separations. In the presence of considerable amounts of potassium, small quantities of other constituents will not materially interfere with the flame and spectroscopic tests. After acidifying with hydrochloric acid, bring a drop of the solution to be tested into the nonluminous flame by means of a platinum wire and observe the color

produced through a Merwin color screen.[1] In the presence of potassium, a distinct reddish-violet coloration will be apparent. This must not be confused with the color caused by large amounts of sodium, which appear bluish-violet through the screen. Comparison with the coloration produced by pure salts is advisable. If necessary, confirm the results by examining the flame in the spectroscope. In the presence of a moderate amount of a volatile potassium compound, a bright red line will be readily seen in the red portion of the spectrum, and a less distinct violet line will be visible far out in the violet rays.

Potassium may be identified by precipitation as cobaltic nitrite. For this purpose place a small quantity of the solution to be examined in a test tube, acidify slightly with acetic acid, add about an equal quantity of the sodium nitrite solution, prepared by dissolving 125 grams of sodium nitrite ($NaNO_2$) in 250 cubic centimeters of distilled water, and about half as much of cobalt nitrate solution, prepared by dissolving 25 grams of cobalt nitrate ($Co(NO_3)_2.6H_2O$) in 100 cubic centimeters of distilled water and adding 50 cubic centimeters of concentrated (glacial) acetic acid. Mix and allow the mixture to stand until effervescence ceases and the cherry-red solution is transparent. If an appreciable amount of potash is present a yellow precipitate will have settled to the bottom of the test tube. By comparing the volume of the precipitate with that produced when a known quantity of potassium chloride is used, an idea of the amount of potash present can be obtained. Ammonium salts produce a similar precipitate.

Potassium chloroplatinate, perchlorate, acid tartrate, picrate, silicofluoride, and phospho-tungstate are all sparingly soluble in water while the corresponding sodium salts are readily soluble. Precipitation of these compounds from solution may be used in the identification of potassium.

Silicate rocks and minerals may be tested for potash by mixing the finely powdered material with an equal quantity of pure calcium carbonate, moistening with hydrochloric acid, and examining a small amount of the wet mixture on a platinum loop in the flame.

### Detection of Alkali Hydroxides and Carbonates

**Test for Hydroxide.** — Dissolve a small amount of the material in water, that is free from carbonic acid ($CO_2$) and add barium chloride solution in such amount that the $BaCl_2$ will be about five times the weight of the sample taken. Filter and add phenolphthalein indicator to the filtrate. A pink or reddish color indicates hydroxide in the sample.

[1] The Merwin color screens are manufactured and sold by G. M. Flint, 84 Wendell Street, Cambridge, Mass., at 25 cents apiece, and are far superior to the ordinary cobalt glass.

**Test for alkali carbonates, bicarbonates or hydroxides in mixtures.** — *A*. Dissolve about one gram of the material in $CO_2$ free water. Add phenolphthalein indicator and titrate with N/10 acid until the color is just destroyed. Note the exact number of cc. of the acid required, and record this as " A."

*B*. To the solution obtained by titration in " A " add methyl orange indicator and continue the titration with the standard acid until a yellowish red color is obtained. Note the exact number of cc. of the acid required and record this as " B."

If " A " = " B " only $Na_2CO_3$ is present.

If " A " titration end-point is acid also to methyl orange, i.e. if a drop or so of the acid changes the yellow to yellowish-red color in the titration following " A " then only NaOH is present.

If " A " is greater than " B " then NaOH and $Na_2CO_3$ are present.

If " A " is less than " B " then $Na_2CO_3$ and $NaHCO_3$ are present.

### Preparation and Solution of Sample

**Procedure for Rocks and Other Insoluble Mineral Products.** — For silicate rocks and other silicious material, bring the alkalies into solution, according to the J. Lawrence Smith or the hydrofluoric acid method, as directed on pages 473 and 475. In the case of alunite prepare the solution as directed on page 475. For products which are dissolved by hydrochloric acid, effect the solution by acid digestion, expel the excess of acid by evaporation, and remove other consitutents as directed under Separations.

**Procedure for Soils.** — Digest 10 grams of moisture-free soil with 100 cc. of hydrochloric acid of a constant boiling-point (sp.gr. 1.115) in a 300 cc. Erlenmeyer flask fitted with a ground-glass or rubber stopper and a reflux condenser. Digest continuously for ten hours on the steam bath, shaking the flask every hour. After settling, decant the solution into a porcelain dish. Wash the insoluble residue onto a filter with hot water, and continue the washing until free from chlorides, adding the washings to the original solution for evaporation. Oxidize the organic matter present in the solution with a few drops of nitric acid and evaporate to dryness on a water bath. Moisten with hydrochloric acid and dissolve in hot water and evaporate a second time to complete dryness and until the excess of hydrochloric acid is completely removed. Moisten the cooled residue with strong hydrochloric acid and dissolve in hot water. Filter into a 250-cc. graduated flask, wash free from chlorides, and dilute to the mark. Use an aliquot of 100 cc. for the determination of the alkalies.

**Procedure for Fertilizers.** — *Potash salts.* — Boil 10 grams of the sample with 300 cc. of water for thirty minutes, wash into a 500 cc. graduated flask, cool, dilute to the mark, mix and pass through a dry filter. Determine the potassium in a 25 cc. aliquot representing 0.5 gram of the original substance, according to either the modified chloroplatinate or the Lindo-Gladding method.

*Mixed fertilizers.* — Boil 10 grams of the sample with 300 cc. of water for thirty minutes, and wash into a 500 cc. graduated flask. Add to the hot solution a slight excess of ammonia and sufficient ammonium oxalate to precipitate all the lime, cool, dilute to the mark, mix, and pass through a dry filter. Evaporate 50 cc. of the filtrate to dryness and ignite gently to remove ammonium salts. Dissolve in water, filter, and determine the potassium according to the modified chloroplatinate or the Lindo-Gladding method.

*Organic compounds.* — When it is desired to determine the total potash in organic substances such as cottonseed meal, tobacco stems, etc., saturate 10 grams with strong sulphuric acid, and ignite in a muffle at low red heat to destroy organic matter. Add a little strong hydrochloric acid, warm slightly to loosen the mass from the dish, dissolve in water, filter, and determine the potassium according to the modified chloroplatinate or the Lindo-Gladding method.

If for any reason it is desired to use either the chloroplatinate or the perchlorate method in the determination of potassium, interfering substances, including sulphates, must first be removed from the solution.

**Procedure for Ashes of Plants.** — Boil 20 grams of the sample with 300 cc. of water for thirty minutes, filter into a 500 cc. flask, and wash the residue thoroughly with hot water. Cool, dilute to the mark and mix. Take aliquots for the determination of the alkalies. The solution may also be prepared by digestion with hydrochloric acid.

**Procedure for Saline Residues, Soluble Salts, Brines, etc.** — In the case of water-soluble products, a sample should be taken sufficient to give about a half gram of solids. Strong brines should be weighed and not measured.

### Separation of the Alkali Metals from other Constituents

**Separation from the Hydrogen Sulphide and Ammonium Sulphide Groups of Metals.** — The alkali metals are usually weighed as chlorides or sulphates, and in general before undertaking their determination all other bases and acids must first be separated from them. The hydrogen sulphide and the ammonium sulphide groups of metals are seldom to be found in solutions in which the determination of the alkalies is desired. If these are present, however, they may be readily precipitated by means of hydrogen sulphide and ammonium sulphide.

**Separation from Silica.** — Acidify the solution with hydrochloric acid and evaporate it in a platinum or porcelain dish on the water bath until the odor of hydrochloric acid in the dry residue can no longer be detected. Break up the dry mass with a platinum or glass rod, cool, moisten with a minimum amount of concentrated hydrochloric acid, dissolve in a small quantity of water, filter and wash the residue free from chlorides. In the presence of much silica, repeat the operation.

**Separation from Iron, Aluminum, Chromium, Titanium, Uranium, Phosphoric Acid, etc.** — If phosphoric acid is present in amounts insufficient to combine with all the iron, aluminum, etc., or is absent altogether, heat the solution to boiling, add a few drops of nitric acid to oxidize the iron, add gradually an excess of ammonia, boil for a minute or so, allow the precipitate to settle, and filter. Wash the precipitate free from chlorides with hot water.

If phosphoric acid is present in the solution in excess of that required to combine with the iron, aluminum, etc., heat the solution to boiling, oxidize with nitric acid, add a slight excess of ferric chloride solution, and precipitate with ammonia as described above.

When the precipitate is considerable, it should be dissolved in hydrochloric acid, and the precipitation repeated.

If chromates are present, these must first be reduced to the chromic salt. For this purpose, add 10 to 15 cc. of hydrochloric acid and a small amount of alcohol to the solution and heat on the water bath or hot plate for a few minutes. Heat to boiling and precipitate with ammonia as directed above. The reduction may also be done by boiling with sulphurous acid.

**Separation from Sulphates.** — Precipitate the sulphate radical as $BaSO_4$ by the addition of a slight excess of barium chloride to the hot solution as directed on page 542 for the determination of $SO_4$. Remove the excess of barium chloride by addition of ammonia and ammonium carbonate.

**Separation from Barium, Calcium and Strontium.** — To the not too concentrated solution, add a slight excess of ammonia and ammonium carbonate, heat to boiling, allow the precipitate to settle, filter and wash the residue a few times with hot water. Dissolve the precipitate, which is likely to contain small amounts of the alkalies, in a little dilute hydrochloric acid, and repeat the precipitation with ammonia and ammonium carbonate. Filter and wash the residue. Evaporate the combined filtrates to dryness in a platinum or porcelain dish and ignite cautiously at a very faint red heat to remove ammonium salts. Dissolve the residue in a little water, add a few drops of ammonia, ammonium carbonate, and ammonium oxalate, and allow to stand for several hours in order to precipitate the last traces of the alkaline earths. Filter and wash the residue free from chlorides.

**Separation from Iron, Aluminum, Chrominum, Barium, Calcium, Strontium, Phosphates, Sulphates, etc., in One Operation.** — To the hot solution add a slight excess of barium chloride and boil for a few minutes. Then, without filtering off the $BaSO_4$, add an excess of ammonia and ammonium carbonate, heat to boiling, and allow the precipitate to settle. Filter and wash free from chlorides with hot water. After evaporating the filtrate to dryness, removing the ammonium salts by ignition, and dissolving the residue in a little water, precipitate the last traces of barium and calcium by addition of a

few drops of ammonia, ammonium carbonate, and ammonium oxalate. By this procedure a small portion of the alkalies is retained by the precipitate and lost.

**Separation from Boric Acid.** — Acidify the solution strongly with hydrochloric acid and evaporate to dryness. Stir up the residue with 15 to 20 cc. of pure methyl alcohol and cautiously evaporate on a water bath at not too high a temperature. Moisten the residue with a drop or two of concentrated hydrochloric acid, add 15 cc. of methyl alcohol, and again take to dryness. Repeat the evaporation with methyl alcohol a third time. This should be ample for the complete removal of half a gram of $B_2O_3$.

### Separation from Magnesium

**The Barium Hydroxide Method.** — Evaporate the solution, which may contain chlorides, sulphates or nitrates, to dryness and gently ignite to remove ammonium salts. Warm the residue with a small amount of water and treat the hot neutral solution so obtained with baryta water until no more precipitate is formed and barium hydroxide remains in slight excess. Boil, filter and wash the precipitate with hot water. If desired, determine the magnesium in the residue. Treat the filtrate, which contains the alkalies, barium and a trace of magnesium, with an excess of ammonia and ammonium carbonate to remove the barium. Acidify the filtrate with hydrochloric acid and evaporate to dryness, ignite and weigh. This residue will contain a small amount of magnesium which may be determined in an aliquot and a correction applied.

**Remark.** — The barium hydroxide method is applicable in the presence of lithium.

**The Ammonium Phosphate Method.** — To the hot solution, add an excess of ammonia and ammonium chloride, and precipitate the magnesium by adding a slight excess of ammonium phosphate. Allow the mixture to stand an hour or so, filter and wash the residue with 2% ammonia solution. Expel most of the free ammonia from the filtrate by evaporation, acidify very slightly with hydrochloric acid, and add an excess of ferric chloride solution, which should color the solution slightly yellow. Neutralize the solution with ammonium carbonate, heat to boiling, and filter off the basic ferric phosphate, washing the residue with hot water. Evaporate the filtrate to dryness, ignite to expel ammonium salts, and determine the alkalies in the residue. Magnesium may also be separated by precipitation as magnesium ammonium arsenate or magnesium ammonium carbonate.

### Separation of the Alkali Metals from One Another

**Separation of Sodium from Potassium.** — After weighing the sodium and potassium together as chlorides, dissolve the residue in water and precipitate the potassium as chloroplatinate or perchlorate according to one of the methods detailed under Determination of Potassium.

**Separation of Lithium from Sodium and Potassium.** — Extract the dry chlorides with amyl alcohol as prescribed under the Gooch method, or with alcohol saturated with hydrochloric acid gas as detailed under the Rammelsberg method.

**Separation of Lithium and Sodium from Potassium, Rubidium, and Caesium.** — Precipitate the potassium, rubidium, and caesium as chloroplatinates as described under the chloroplatinate method for the estimation of potassium. Evaporate the filtrate to dryness and ignite gently with a little oxalic acid to reduce the platinum, or else dissolve the residue in water and pass a current of hydrogen through the hot solution to reduce the platinum. In any case, filter off the reduced platinum and determine lithium and sodium in the filtrate.

## METHODS FOR DETERMINATION OF POTASSIUM

### THE MODIFIED CHLOROPLATINATE METHOD [1]

**Application.** — The method is applicable in the presence of chlorides, sulphates, phosphates, nitrates, carbonates, borates and silicates, salts of sodium, barium, calcium, strontium, magnesium, iron and aluminum, and is especially suited for the estimation of potassium in salines, potassium salts, and fertilizers in which only the potassium is desired.

**Principle.** — On evaporating a solution containing potassium with a slight excess of chloroplatinic acid, the potassium is completely transformed into potassium chloroplatinate which is insoluble in strong alcohol, while any of the other chloroplatinates which may be formed are either dissolved or decomposed by alcohol, so that the excess of chloroplatinic acid may be readily removed. After dissolving the $K_2PtCl_6$ along with any other soluble salts contained in the residue in hot water, the platinum is precipitated from the solution by magnesium, and from the weight of platinum so obtained, the amount of potassium present is calculated.

**Procedure.** — To the solution slightly acidified with hydrochloric acid, add chloroplatinic acid solution slightly in excess of that necessary for the complete precipitation of the potassium present and evaporate the solution on the steam bath to a syrupy consistency, i.e., until solidification occurs on cooling. Flood the cooled residue with a small quantity of alcohol of at least 80% strength, grind thoroughly with a pestle made by enlarging the end of a glass rod, and allow to stand one-half hour. The alcoholic solution should be colored if an excess of chloroplatinic acid has been used. Pour the liquid through a small filter, using suction if desired, and before adding more alcohol, rub up the residue again with the pestle. Now continue the washing by decantation with small portions of alcohol until the wash liquid becomes colorless. Three or four washings usually suffice. Transfer the precipitate to the filter and wash two or three times with alcohol.

Dissolve the precipitate of $K_2PtCl_6$ along with any other soluble salts present in hot water, washing it through the filter into a beaker of convenient size. To the hot solution add about 4 cc. of concentrated HCl and approximately 0.5 gram of magnesium ribbon pressed into the form of a ball for every 0.1 gram of potassium present, stirring the solution and holding the magnesium at the bottom of the beaker by means of a glass rod. A lump of stick magnesium weighing about 0.4 gram is preferable to the ribbon. When the action has practically ceased, add a few cc. of hydrochloric acid and allow the fluocculent platinum to settle, preferably by allowing the beaker to set for an

[1] Hicks, J. Ind. Eng. Chem., 5, 650, 1913.

hour on the hot plate. The supernatant liquid should be perfectly clear and limpid like water if reduction is complete. To make sure, add more magnesium, in which case the solution will darken if reduction be incomplete. To the completely reduced solution, add concentrated hydrochloric acid, and boil to dissolve any basic salts, filter on paper or a Gooch, wash thoroughly with hot water, ignite in platinum or porcelain and weigh.

$$Pt \times .4006 = K \text{ or } \times .4826 = K_2O.$$

**Remarks.** — If the solution contains very large amounts of iron, aluminum, or silicon, it is preferable to remove the greater part of these before proceeding to the determination of potassium. Care should be taken to insure the complete removal of the soluble chloroplatinates from the residue without the use of an excessive amount of alcohol, and also that the subsequent reduction of the potassium chloroplatinate with magnesium be complete.

### THE CHLOROPLATINATE, LINDO-GLADDING METHOD [1]

**Application.** — This method is applicable in the presence of chlorides, sulphates, and phosphates of the alkalies and magnesium.

**Principle.** — The potassium is precipitated as $K_2PtCl_6$, and the soluble chloroplatinates removed by washing with 80% alcohol. The impurities in the precipitate are then washed out by a strong solution of ammonium chloride saturated with $K_2PtCl_6$, and the wash solution is removed by again washing with alcohol. The purified $K_2PtCl_6$ is finally dried and weighed.

**Procedure.** — To the solution, slightly acidified with hydrochloric acid, add an excess of chloroplatinic acid solution, and evaporate on the water bath to a thick paste. Treat the residue with 80% alcohol, avoiding the absorption of ammonia. Wash the precipitate thoroughly with 80% alcohol both by decantation and on the filter, continuing the washing after the filtrate is colorless. Wash finally with 10 cc. of ammonium chloride solution prepared as follows: Dissolve 100 grams of pure ammonium chloride in 500 cc. of water, add from 5 to 10 grams of potassium chloroplatinate, and shake at intervals of six to eight hours. Allow the mixture to settle over night and filter. Repeat the washing with successive portions of the ammonium chloride solution five or six times in order to remove the impurities from the precipitate. Wash again thoroughly with 80% alcohol, dry for thirty minutes at 100° C. and weigh as $K_2PtCl_6$. The precipitate should be perfectly soluble in water. Multiply the weight of $K_2PtCl_6$ by 0.161 to obtain the weight of K by 0.194 to obtain $K_2O$ and by 0.307 to obtain KCl.[2]

[1] U.S. Dept. Agri., Bu. Chem. Bull. 107 (revised), 11, 1907.

[2] Instead of using a Gooch crucible, the precipitate may be filtered on paper, dried, washed through the filter with hot water into a weighed platinum dish, evaporated to dryness, and heated at 130° C. to constant weight.

### THE PERCHLORATE METHOD [1]

**Application.** — This method is applicable in the presence of chlorides and nitrates of barium, calcium, magnesium and the alkali metals, and also in the presence of phosphates. Sulphates should not be present.

**Principle.** — The separation depends on the insolubility of potassium perchlorate, and the solubility of sodium and other perchlorates in 97% alcohol.

**Procedure.** — To the neutral or slightly acidified solution, add twice as much perchloric acid as is required to convert all the bases present into perchlorates and evaporate on the water bath with stirring to a syrupy consistency. Add a little hot water and continue the evaporation with constant stirring until all the hydrochloric acid is expelled and heavy fumes of perchloric acid are given off. Avoid excessive loss of perchloric acid. Stir up the cooled mass thoroughly with 20 cc. of 97% alcohol to which 0.2% perchloric acid has been added, but avoid breaking up the potassium perchlorate crystals too finely or else they may pass through the filter. Allow the mixture to settle, and decant the alcohol off through a Gooch crucible. Repeat the washing once by decantation and then warm to remove the alcohol. Dissolve the residue in hot water, add about a half gram of perchloric acid and evaporate again until fumes of perchloric acid are given off. Wash the residue once by decantation and then several times on the filter. Remove the adhering wash-liquid by washing with pure 97% alcohol, dry at 130° C., and weigh. Multiply the weight of $KClO_4$ by 0.2825 to obtain the weight of K by 0.3402 to obtain $K_2O$.

[1] Wense, Zeit. Angew. Chem., 691, 1891; 233, 1892.

## SODIUM

**Sodium, Na, at.wt. 23.00; sp.gr. 0.9735; m.p. 97.6°; b.p. 877.5° C.; oxides $Na_2O$, $Na_2O_2$.**

### OCCURRENCE

Sodium occurs combined in nature, abundantly and widely distributed. It occurs in enormous deposits as sodium chloride, "rock salt," and in solution in sea water, in certain inland lakes, and springs. It occurs as sodium nitrate, as Chili saltpeter, in great deposits of South America. It occurs as a borate. It is found in the plant and animal kingdoms.

**Minerals.** — *Halite*, "rock salt," NaCl, is a vitreous, colorless white, yellow, brown or red (according to impurities, transparent to translucent mineral, having a saline taste. *Borax*, $Na_2B_4O_7.10H_2O$, vitreous to dull, white, gray, bluish or greenish earthy mineral, with a mild though disagreeable alkaline taste. *Cryolite*, $Na_3AlF_6$, a mineral with greasy to vitreous lustre, colorless to white, sometimes reddish or brown, transparent to translucent. *Soda nitre*, $NaNO_3$ "Chili saltpeter," dull to vitreous lustre; white, colorless, gray or yellow; transparent to translucent, salty and cooling taste. *Mirabilite*, Glauber Salt, $Na_2SO_4.10H_2O$. *Natron*, $Na_2CO_3.10H_2O$. *Trona*, $Na_2CO_3.HNaCO_3.2H_2O$.

### DETECTION

Sodium is usually identified by the color which it imparts to the flame or by means of the spectroscope. The solution is prepared as directed under Preparation and Solution of Sample, and is freed from all constituents other than the chlorides of magnesium and the alkalies according to the methods given under Separations. With exceedingly small amounts of sodium, it may be necessary to remove the magnesium also. After acidifying with hydrochloric acid, a drop of the solution is brought into the flame by means of a loop of platinum wire. In the presence of sodium, the flame assumes an intense yellow color, which is usually sufficient to identify the element. The results may be confirmed by examining the flame in the spectroscope, when the characteristic yellow sodium line will be prominent even in the presence of traces of sodium. As a matter of fact, the ever-presence of the sodium line is a hindrance to the success of the method, but by observing the sudden change in the intensity of the line, little trouble will be experienced in detecting exceedingly small amounts of the metal.

Sodium may also be detected by precipitation as sodium pyroantimonate, $H_2Na_2Sb_2O_7.H_2O$, from a sufficiently concentrated neutral or weakly alkaline solution by means of a solution of acid potassium pyroantimonate. The precipitate comes down in granular or crystalline form, and its formation is hastened by rubbing the sides of the vessel with a glass rod. In making this test, magnesium must also be previously removed from the solution.

In waters and soluble salts, it is usually sufficient to test directly the concentrated solution in the flame or spectroscope.

**Preparation of the Solution and Separations.** — See procedures under Potassium pages 462–466.

## METHODS FOR DETERMINATION OF SODIUM

### DETERMINATION AS SODIUM CHLORIDE

Sodium is commonly weighed as NaCl when it is already present as such or after conversion of other forms into the chloride. In the case of salts of volatile acids, such as nitrates for instance, the transformation is made by evaporating the solution to dryness with hydrochloric acid repeatedly or until only the chloride remains. When the sodium is present as a salt of a non-volatile acid, the latter is removed according to the methods under Separations.

Usually the solution in which sodium chloride is to be determined will contain ammonium salts from some previous operation. In such cases, proceed as follows: Evaporate the sodium chloride solution, which must contain no other non-volatile substance, in a platinum dish to complete dryness on the water bath. Cover the dish with a watch-glass, and cautiously dry the residue in an air bath at 110 to 130° C. Make sure that no loss of sodium chloride is sustained by decrepitation during drying and subsequent ignition. Heat the dish and contents over a free flame held in the hand and moved back and forth under the dish in order to remove ammonium salts. But to avoid loss of sodium chloride by volatilization, take care not to heat the dish to more than a faint redness in any one spot and not to raise the temperature of the salt above incipient fusion. Cool the residue, dissolve it in a little water, and filter from the carbonaceous matter into a weighed platinum dish. Acidify the filtrate with hydrochloric acid and evaporate it to dryness on the water bath. Dry the residue at 100 to 130° C. in an air bath, ignite cautiously over a free flame, taking the precautions mentioned above to prevent loss of sodium chloride, cool in a desiccator, and weigh.

### DETERMINATION AS SODIUM SULPHATE

Sodium is often determined by weighing as $Na_2SO_4$ when it is present as such or after conversion of other forms into the sulphate. In the case of salts of volatile acids, the change into the sulphate is made by simply evaporating the solution with a slight excess of sulphuric acid. With salts of non-volatile acids, the transformation is effected according to the methods under Separations. When the sodium is present as an organic salt, the substance is moistened with concentrated sulphuric acid and carefully heated over a free flame until fumes cease to come off. The residue is dissolved in water and filtered from the carbonaceous matter.

As a rule the solution in which sodium sulphate is to be determined will contain an excess of sulphuric acid. In such cases, evaporate the solution to dryness in a weighed platinum dish, and cautiously ignite the dry residue until fumes cease to come off. Cool, add a

lump of ammonium carbonate to the contents of the dish, and ignite a second time at dull red heat until no more fumes are given off. Cool in a desiccator and weigh as $Na_2SO_4$. Repeat the ignition with the addition of ammonium carbonate until a constant weight is obtained.

In case an excess of sulphuric acid is not present, evaporate the solution to dryness in a weighed platinum dish, ignite, and weigh as $Na_2SO_4$.

### Determination by Difference

Ordinarily sodium and potassium are weighed together as chlorides or sulphates as detailed above for sodium. Potassium is then determined.

## DETERMINATION OF THE ALKALIES IN SILICATES

### J. Lawrence Smith method [1]

**Principle.** — By heating the substance with 1 part of ammonium chloride and 8 parts of calcium carbonate, and leaching the sintered mass with water, the alkalies are obtained in solution in the form of chlorides along with some calcium, while the remaining metals are for the most part left behind as insoluble oxides, and the silica is changed to calcium silicate.

**Procedure.** — Titrate 0.5 gram of the finely powdered mineral with an equal quantity of pure ammonium chloride in an agate mortar, add 3 grams of precipitated calcium carbonate [2] and mix intimately with the former. Transfer the mixture to a platinum crucible (preferably the J. Lawrence Smith alkali crucible), rinse the mortar with 1 gram of calcium carbonate and add to the contents of the crucible. Place the covered crucible in a slightly inclined position with the top protected from the heat of the flame. This can be done by setting the crucible in a hole in a cylinder of fire clay, as shown in Fig. 96. Gradually heat the crucible over a small flame until no more ammonia is evolved, but avoid heating sufficiently to cause the evolution of ammonium chloride. This should require about fifteen minutes. Then raise the temperature until finally the lower three-fourths (and no more) of the crucible is brought to a red heat, and maintain this

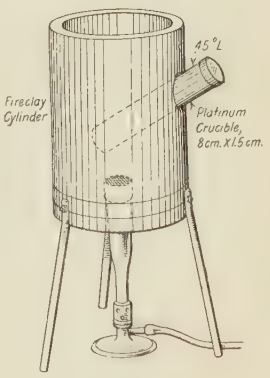



Fig. 96

[1] Am. J. Sci. (3), 1,269, 1871; Hillebrand, U.S. Geol. Survey Bull. 422, 171, 1910.

[2] Blank determinations should be run on the calcium carbonate, and corrections made for its alkali content.

temperature for one hour. Allow the crucible to cool and remove the sintered cake by gently tapping the inverted crucible. Should this not be possible, digest the mass a few minutes with water to soften the cake, and then wash it into a large porcelain or platinum dish. Heat the covered dish with 50 to 75 cc. of water for half an hour, reduce the large particles to a fine powder by rubbing with a pestle in the dish, and decant the clear solution through a filter. Wash the residue four times by decantation, transfer it to a filter, and wash with hot water until a few cc. of the washings give only a slight turbidity with silver nitrate. To make sure the decomposition of the mineral has been complete, treat the residue with hydrochloric acid. No trace of undecomposed mineral should remain undissolved.

The aqueous extract obtained in the above operation contains the chlorides of calcium and the alkalies. To remove the calcium, treat the solution with ammonia and ammonium carbonate, heat to boiling, filter and wash the residue. As this precipitate invariably retains some alkali salts, it should be dissolved in hydrochloric acid and the precipitation repeated. Evaporate the filtrate to dryness in a platinum or porcelain dish, and expel the ammonium salts by gentle ignition over a moving flame. After cooling, dissolve the residue in a little water, and add a few drops of ammonia and ammonium oxalate to remove the last trace of calcium. After standing several hours, filter off the calcium oxalate, receive the filtrate in a weighed platinum dish, evaporate to dryness and ignite gently to remove ammonium salts. Moisten the cooled mass with hydrochloric acid to transform any carbonate into chloride, and again evaporate to dryness and ignite. Cool in a desiccator and weigh the combined chlorides. Dissolve in water, and if an insoluble residue remains, filter off, weigh and deduct from the weight of the chlorides. Determine the potassium by one of the methods already described, and obtain the value for sodium by difference.

### THE HYDROFLUORIC ACID METHOD

**Procedure.** — Weigh out a half-gram sample of the finely powdered mineral, place in a small platinum dish or a large platinum crucible, moisten with a few drops of water, and add about 10 cubic centimeters of hydrofluoric acid and about 2 cubic centimeters of dilute sulphuric acid. Hold the dish with the tongs and heat it and its contents cautiously over the free flame for a few minutes. Evaporate the solution on the steam bath to complete dryness, and during this evaporation agitate the solution occasionally by giving the dish a gyratory motion with the tongs. This treatment is nearly always sufficient to decompose the mineral, but if decomposition seems incomplete add more hydrofluoric acid and evaporate a second time, agitating the mixture frequently. With refractory silicates it may be desirable to digest the mineral with the acid mixture in a covered crucible for an hour or so. Heat the dish and its contents on a radiator[1] to expell the excess of hydrofluoric and sulphuric acids. Cover the residue with dilute hydrochloric acid and digest on a steam bath until solution is complete, adding more water and acid if necessary. Flakes of organic matter which remain undissolved may be neglected. Remove the iron, aluminum, calcium, etc., by the methods described under "Separations." Finally weigh the magnesium, sodium, and potassium as sulphates and determine the potassium according to the modified chloroplatinate or Lindo-Gladding method. An alternative procedure is to remove sulphates and magnesium also as described under "Separates," weigh the alkalies as chlorides, and determine the potash by any of the methods already described. It should be noted however that potash is carried down with barium sulphate, and the loss thus occasioned may be appreciable.

[1] Hillebrand, W.F., U.S. Geol. Survey Bull. 422, p. 31, 1901 (reprinted, 1916). A large porcelain crucible serves well as a radiator for this purpose.

## LITHIUM

**Lithium, Li, at.wt. 6.94; sp.gr. 0.534; m.p. 186°; b.p. >1400°C.; oxide $Li_2O$.**

### OCCURRENCE

Lithium is found combined in nature, widely distributed but always in very small quantities. It is found in mineral waters, in ashes of many plants, notably tobacco and beet.

**Minerals.** — *Spodumene*, $LiAl(SiO_3)_2$, a mineral of vitreous to stony or dull lustre, grayish white, occasionally green or pink, brittle, transparent to opaque. (Hardness 6.5–7.) *Lepidolite*, $KLi.Al(OH)_2AlF_2.Al(SiO_3)_3$, pearly, pink or lilac, rarely violet, gray, yellowish or white, translucent mineral. *Amblygonite*, $Li(AlF)PO_4$, vitreous to dull lustre, white or light tints, brittle, translucent to nearly opaque mineral with hardness of 6. Petalite, $LiAl(Si_2O_5)_2$ Triphylite, $Li(Fe,Mn)PO_4$.

### Detection of Lithium

Bring the sample into solution as directed under Preparation and Solution of Sample, and separate the alkali chlorides from other constituents according to the methods under Separations. Digest the dry chlorides with amyl alcohol or with a mixture of absolute alcohol and ether, filter, and evaporate the filtrate to dryness. Moisten the residue with dilute hydrochloric acid and examine it in the spectroscope. A bright red band and a faint orange line make up the flame spectrum of lithium. These lie between the sodium line and the red potassium line and are easily recognized.

Lithium salts impart a carmine-red color to the flame, which is obscured by sodium, and by large amounts of potassium. But by the proper use of a color screen, the lithium flame may be recognized in the presence of large amounts of sodium.

Confirmation of the presence of lithium may be had by the formation of the sparingly soluble lithium phosphate or lithium fluoride.

## METHODS FOR DETERMINATION OF LITHIUM

### THE GOOCH METHOD [1]

**Principle.** — Lithium chloride is readily soluble in amyl alcohol, while sodium and potassium chlorides are not.

**Procedure.** — Concentrate the solution as far as possible by evaporation, transfer it to a 50 cc. Erlenmeyer flask, add a small amount of amyl alcohol and heat cautiously on an asbestos plate until the water has been expelled and the boiling-point of the solution rises to about that of pure amyl alcohol (132° C.). To prevent bumping during this treatment, pass a current of dry air through the solution. When all the water has been removed, the sodium and potassium chlorides, together with some LiOH, will separate from the solution. Decant the solution through a filter and wash the residue several times with hot amyl alcohol. Moisten the residue with dilute hydrochloric acid, dissolve in a little water and repeat the extraction with amyl alcohol. If much lithium chloride is present, it will be necessary to repeat the extraction with amyl alcohol three or four times. Evaporate the combined filtrates and washings to dryness and dissolve in a little dilute sulphuric acid. Filter from the carbonaceous matter into a weighed platinum dish, evaporate to dryness, and remove the excess of sulphuric acid by gentle heating. Ignite the residue at dull redness, cool in a desiccator, and weigh as $Li_2SO_4$.

**Remarks.** — For very accurate work, account must be taken of the fact that the lithium sulphate obtained according to the procedure just described always contains small amounts of potassium and sodium sulphates, if these metals were originally present. To correct for this, deduct 0.00041 gram for every 10 cc. of the filtrate exclusive of the washings in case only sodium chloride was present, or 0.00051 if only potassium chloride was present, and 0.00092 if both sodium and potassium chlorides were present.

[1] Proc. Am. Acad. Arts. Sci., 22 (N.S. 14), 177, 1886.

### THE RAMMELSBERG METHOD

**Principle.** — Anhydrous lithium chloride is soluble in equal parts of alcohol and ether which have been saturated with hydrochloric acid gas, while the chlorides of sodium and potassium are practically insoluble in this mixture.

**Procedure.** — Evaporate the solution of the chlorides to dryness in a small flask provided with a two-hole stopper. During the evaporation, pass a current of dry air through the flask. Place the flask containing the dry residue in an oil or air bath and heat for half an hour at 140 to 150° C., during which time pass dry hydrochloric acid gas through the flask. Cool in a current of hydrochloric acid gas, treat the residue with a few cc. of absolute alcohol which has been saturated with hydrochloric acid gas, and add an equal volume of absolute ether. Close the flask tightly and allow it to stand with frequent shaking for twelve hours. Pour the solution through a filter, wet with the alcohol-ether mixture and wash the residue three times by decantation with the alcohol-ether mixture. Add a few more cc. of the alcohol-ether saturated with hydrochloric acid gas to the contents of the flask and allow to stand again for twelve hours. Pour the liquid through a filter, and wash the residue by decantation with the alcohol-ether mixture until the residue tested in the spectroscope shows the complete absence of lithium. Carefully evaporate the combined alcohol-ether extract to dryness on a lukewarm water bath. Dissolve the residue in sufficient dilute sulphuric acid to convert all the lithium into the sulphate, transfer the solution to a weighed platinum dish, evaporate to dryness on the water bath, and finally ignite gently. Cool the residue in a desiccator and weigh as lithium sulphate.

Note. Lithium may also be precipitated and weighed as $Li_3PO_4$,[1] or it may be precipitated as LiF [2] and then changed into the sulphate and weighed.

[1] Mayer, Ann. Chem. Pharm., **98**, 193, 1856. Merling, 3 Anal. Chem., 18, 563, 1879.

[2] Carnot, 3 Anal. Chem., **29**, 332, 1890.

### Determination as Lithium Chloride

Lithium may be weighed as LiCl. The procedure is practically the same as that described for sodium, but since lithium chloride is very hygroscopic, this salt must be weighed out of contact with the air. For this purpose the lithium chloride is ignited in a platinum crucible, cooled in desiccator, and the crucible and contents weighed in a glass-stoppered weighing bottle.

### Determination as Lithium Sulphate

Lithium is weighed preferably as $Li_2SO_4$. The procedure is the same as that described for sodium, but since lithium bisulphate is easily broken up on heating, it is not necessary to ignite with ammonium carbonate.

### Spectroscopic Method [1]

Dissolve the lithium salt containing small amounts of sodium and potassium resulting from the separation by the Gooch or Rammelsberg methods in 5 or 10 cc. of water, depending on the amount of lithium present. Gradually add measured amounts of this solution to a known volume of water — testing the solution from time to time in the spectroscope — until the lithium line appears. When only traces of lithium are present, it is better to dissolve the lithium salt in a little water and dilute to the vanishing point of the lithium line. Make the spectroscopic examination as follows: Prepare a loop by winding a platinum wire four times around a No. 10 wire. Plunge the loop into the solution, and remove with the axis parallel to the surface of the water. Evaporate the drop to dryness carefully, ignite in the Bunsen flame, and observe through a good spectroscope.

Before undertaking the determination, standardize the instrument and platinum loop by carrying out the determination with known amounts of lithium.

The method gives satisfactory results when only an approximation is desired. For weighable amounts of lithium, the Gooch method is preferable.

[1] Skinner and Collins, U.S. Dept. Agri. Bu. Chem., Bull. 153. A good bibliography is included in this bulletin.

## COMBINATIONS

### Determination of Sodium, Potassium, and Lithium in the Presence of One Another

Weigh the combined bases as sulphates, observing the precautions detailed under Determination of Sodium, dissolve in water and dilute to definite volume. In one portion determine the potassium and in a second portion determine the lithium by the Gooch or Rammelsberg method. Obtain the value for the sodium by difference.

### Determination of Sodium and Potassium by Indirect Method

After removing all other constituents, weigh the sodium and potassium as chlorides. Dissolve the weighed residue in water and determine the chlorine gravimetrically by precipitation as AgCl or volumetrically by titration with standard silver nitrate (potassium chromate indicator). From the weight of the combined salts and the weight of the chlorine, calculate the amount of sodium and potassium as follows:

$x$ = weight of NaCl + KCl. $y$ = weight of Cl.

Then $\mathrm{Na} = 3.004y - 1.428x$; $\mathrm{K} = 2.428x - 4.004y$.

The method is satisfactory when sodium and potassium are present in about equal quantities.

### Determination of Magnesium, Sodium and Potassium in the Presence of One Another

In the usual course of analysis, magnesium, sodium and potassium are separated as chlorides from all other constituents. Instead of going through the tedious process of separating the magnesium from the alkalies, the magnesium, sodium, and potassium may be accurately determined in the presence of each other as follows:

Treat the solution containing these constituents with slightly more than enough sulphuric acid to convert all three bases into sulphates; evaporate it to dryness on the water bath, and ignite gently at first and then at dull red heat to break up bisulphates and expel the excess of sulphuric acid. To hasten the decomposition of the bisulphates, cool, add a lump of ammonium carbonate, and heat a second time. Cool in a desiccator and weigh. Repeat the heating with the addition of ammonium carbonate until a constant weight is obtained. Dissolve the residue in water and dilute to definite volume. Determine the potassium in one portion according to one of the methods described above, and the magnesium in a second portion. Deduct the weight of magnesium and potassium sulphates from the weight of the combined sulphates to obtain the amount of sodium sulphate.[1]

[1] The greater portion of the material in this chapter was contributed by Dr. W. B. Hicks, Director of the Analytical Department of The Solvay Process Co.

## RUBIDIUM AND CAESIUM

**Rubidium, Rb, at.wt. 85.45; sp.gr. 1.532; m.p. 38.5°; b.p. 696° C.; oxides $Rb_2O$, $Rb_2O_2$, $Rb_2O_3$, $Rb_2O_4$.**

**Caesium, Cs, at.wt. 132.81; sp.gr. 1.87;m.p. 26.37°; b.p. 670° C.; oxides $Cs_2O$, $Cs_2O_2$, $Cs_2O_3$, $Cs_2O_4$.**

### OCCURRENCE

Occur together, found only in combined state, widely distributed but in very small amounts. Found in plant ashes and in several minerals, commonly associated with salts of potassium. Carnallite contains about 0.025% of rubidium; caesium is much rarer than rubidium; the mineral *pollucite* (Elba Isl.) is a silicate of aluminum and caesium and contains about 34% caesium oxide. Other minerals — rhodizite, Al, K, Cs, borate.

### Detection of Rubidium and Caesium

In the usual course of analysis, these rare elements are separated along with sodium, potassium, and lithium from all other bases. In order to detect rubidium and caesium, extract the dry chlorides of the alkali metals with a few drops of hydrochloric acid and 90% alcohol. This will dissolve most of the rare alkalies along with some sodium and potassium. Evaporate the solution to dryness, dissolve in a very small amount of water, and add chloroplatinic acid solution. Rubidium, caesium, and potassium chloroplatinates will be precipitated. Filter and wash the residue repeatedly with hot water to remove the potassium salt, which is much more soluble than rubidium and caesium chloroplatinates. During this treatment, examine the residue from time to time in the spectroscope. As the rubidium and caesium salts are concentrated through washing, their spectra will gradually become visible. (See Plate II Emmissions–Spectra.)

## RADIUM

### DETECTION

Radium discharges the electroscope of the alpha ray instrument. However, other radioactive elements do also. There are only three elements that give a gas called emanation as a product. These elements are actinium, radium and thorium. They can all be distinguished by collecting the gas and observing its rate of decay. The time required for one half of the gas to decay is known as the half-

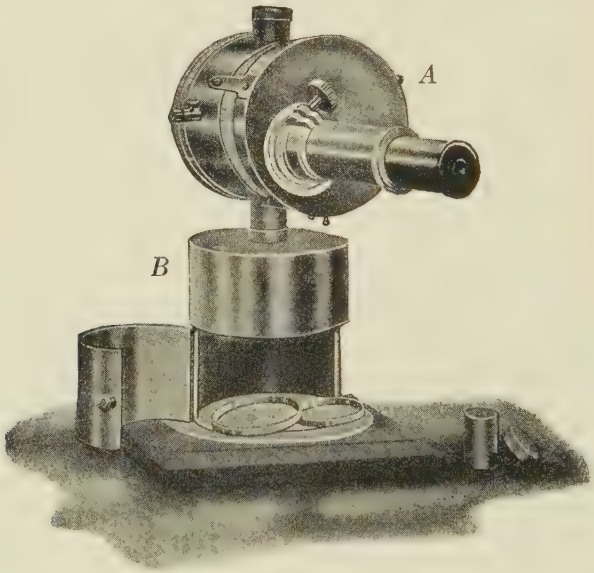



FIG. 97.

period. The half-period of actinium emanation is 3.9 sec., radium emanation 3.85 days, thorium emanation 54 sec. In preparing samples for the alpha ray test they should be ground to about the same mesh. If the sample causes the leaf to move faster than it moves when the chamber is empty, the specimen is radioactive. The time is taken with a stop-watch.

### ESTIMATION

Radium is determined by the following methods: I, Alpha Ray; II, Emanation; III, Gamma Ray. The determination with the alpha

ray instrument is only approximate and depends on having the samples in the same physical condition as much as possible. The discharge of the leaf is influenced by the fineness of the sample. Also the compound that the element is found in makes a difference. The emanating power of radium chloride is greater than that of radium sulphate, or oxalate. This method is used in the mining camps because it is simple and requires very little equipment. The emanation method is more accurate and is usually used at the plant and laboratory. The gamma ray method is used when the sample cannot be removed from its container, and also for very high grade material. Tubes of emanation prepared for therapeutic use are determined in this way.

### THE ALPHA RAY METHOD

The alpha ray instrument consists of an electroscope head *A* (Fig. 97) and the chamber *B*. Head *A* contains an aluminum or gold leaf attached to a metal rod and a reading telescope so placed as to read the deflection of the leaf when charged. *B* is the chamber to receive the sample. A spring from the metal rod in *A* connects this with a rod which extends into *B*. On the end of the latter is placed a disk. The rays discharge the leaf through this disk and rod. The rod in the chamber is insulated from the case with amberoid, made by subjecting amber powder to great pressure. *A* is charged by means of a battery, or an ebonite rod can be used. The battery is made by connecting seventy-five to a hundred French cells (or Eveready Tungten No. 703) of about five volts each in series. It is best to ground the negative end and connect *A* by a floating wire to the positive pole of the cell which will give the desired deflection of the leaf. The case of the chamber is connected to the ground wire. A tube of distilled water is placed in the circuit to prevent the shorting of the batteries. Care should be taken not to charge the leaf enough to throw it against the case. The "natural Leak" is found by taking the time for the leaf to move over forty divisions, and calculating the divisions per second. Less than forty divisions may be taken if the time for forty divisions is quite long. If the leaf moves at the same rate over the whole scale, any part may be taken. The sample is placed in the plate for solids, and this is made exactly level full. The plate containing the sample is placed in a pan to protect the instrument from receiving active matter. The pan with its contents is now placed in the chamber *B*. As the charged leaf passes 8 (or some other chosen starting place) the stop watch is started. The watch is stopped at 4. The rate of discharge is calculated in divisions per second, and the natural leak is subtracted. A standard is run in exactly the same way. Since the rate of discharge is directly proportional to the amount of radium present, the amount of radium in the sample may be found by comparing its rate of discharge with that of the standard. This method gives approximate results. If the samples are of the same general character, the results may be in very good agreement, checking those obtained by the emanation method very closely.

## EMANATION METHOD

**I. Carbonate Fusion.** About 2 grams of a mixture of sodium and potassium carbonates are placed in a platinum boat about 2 in. long $\frac{1}{2}$ in. wide and $\frac{1}{2}$ in. deep. Larger boats may be used for low grade samples where large amounts are taken for analysis. From 0.05 to 1 gram of the sample should be weighed in the boat. The boat is now filled level full of the fusion mixture. The fusion is made over flame, or better, in an electric furnace at about 1000° C. The boat should be put in the furnace while the furnace is cool. This will allow the fusion to dry and melt slowly, thus tending to prevent "boiling" over. The analyst will learn by practice how fast to heat up the furnace. When thoroughly fused and while still at the highest temperature, suddenly chill the fusion by dipping the boat in water, being careful not to allow water to run into the boat and wet the fusion. This chilling causes the mass to draw away from the boat and in the acid treatment slip out of the boat. The mass is also made more porous so that the acid attacks it much better. If very little silica is present, the chilling is not necessary. However, it does no

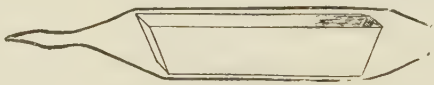


FIG. 98.

harm. The boat with the fusion is sealed in a glass tube as shown in Fig. 98. The tube should be no larger than necessary. A number of tubes should be prepared in advance by having one end sealed. After standing from one to five or more days (this time depends on the amount of radium present and on the time the result is demanded, the fourth day is usually about right; this gives a little more than a 50 per cent recovery of the emanation) the emanation surrounding the boat is drawn into an evacuated chamber. The chamber may be evacuated by means of an aspirator on the water faucet or by a pump. To draw the emanation from the tube to the evacuated chamber a rubber tube is placed on one end of the sealed tube and connected to the chamber with a capillary tube intervening to prevent broken glass from being drawn into the chamber, and a glass stopcock is connected by a rubber tube on the other end. The tip of the sealed tube next to the chamber is broken with a pair of pliers and the stopcock of the chamber opened for an instant. The other tip is broken and the glass stopcock opened for an instant. The stopcock of the chamber is opened again and closed after an instant. Air is let in through the glass stopcock again. After air is taken through about three times the chamber is ready to receive the emanation from the burette. It is necessary to use only a small part of the vacuum to

draw the emanation from the sealed tube. The tube is broken and the boat is folded in a filter paper in such a manner that the paper will hold the boat in the neck of the flask until the flask is connected with the apparatus as shown in Fig. 99. About 4 in. of a stick of sodium

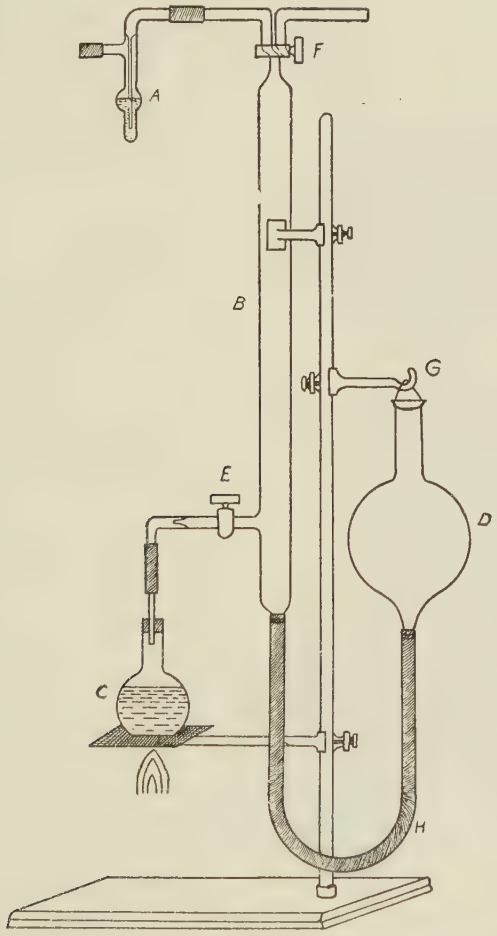



FIG. 99.

hydroxide is placed in the leveling bulb *D*. Boiling water is poured on this and the solution is raised in the burette about three-fourths of its height, having stopcock *E* closed and *F* open. *F* is now closed and the leveling bulb hung on hook *G*. Flask *C* contains 1–1 $HNO_3$; or if the fusion is hard to disintegrate 3 parts of acid to 2 of water

is used. The boat is shaken into the nitric acid and stopcock *E* opened immediately. A Bunsen burner flame is applied to the flask and the acid brought to boiling. The boiling is continued for 10 to 30 minutes according to the nature of the fusion. The heating must be regulated so that the solution in the burette is not driven too low. If the flask is heated too strongly the gas may be prevented from escaping through tube *H* by raising leveling bulb *D*. The burette is now connected to the chamber by means of a micro-drying bulb *A* containing sulphuric acid. The stopcock of the chamber is opened very slightly. Then the stopcock of the burette is opened slowly but fully. The stopcock of the chamber is now regulated till the flow of gas is such that the liquid in the burette rises steadily but not too fast. When the liquid rises to the stopcock the stopcock is turned and air let in till the level is about one-fourth down the tube. The air is drawn into the chamber till the liquid again reaches the stopcock. The air is again let in as before. The stopcock is opened into the chamber again and the liquid poured out of the leveling bulb. Air is drawn through the column till the chamber is full. The burette is disconnected, and the chamber set away to be read at the end of three hours. Just before time to make the reading the electroscope head is placed on the chamber and charged for fifteen minutes, and the chamber is opened to atmospheric pressure by opening the stopcock for only an instant, Fig. 100. From three to ten readings with the stop watch are taken over forty small divisions, say from 8 to 4. The temperature and pressure are noted. If these vary greatly from the conditions at which the instrument was standardized, the correction of the discharge must be made. The rate of discharge will be

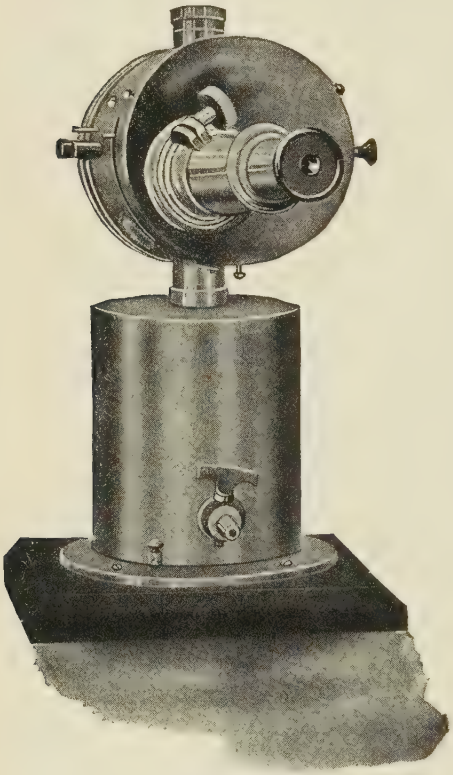


Fig. 100.

proportional to the pressure and inversely proportional to the temperature. The discharge is calculated in divisions per second. The natural leak, or still better, the blank is subtracted from this. This discharge is compared with that of a standard.

**Example of a Determination and Calculation.**

0.5 g. of sample sealed Oct. 1 at 5:00 P.M.
Boiled off Oct. 5 at 8:30 A.M.
Time of recovery 3 days, 15½ hours

| | | | |
|---|---|---|---|
| Recovery factor for 3 days, | 15 hr. | 0.47926 | See table. |
| | ½ hr. | 0.00193 | |
| | | 0.4812 | |
| log. of | | 0.4812 | − 1.6822 |
| colog. of | | 0.4812 | .3178 |

A — II Time of discharge over 40 divisions of head A on chamber II. 92.5 sec.

B — II Time of discharge over 40 divisions of head B on chamber II. 100 sec.

1.6021 log. of 40
1.9661 log. of 92.5

| | | |
|---|---|---|
| − 1.6360 | − 1.6330 | log of 0.4295 |
| .4325 | − 9.9450 | standardization of instrument |
| .0030 blank | .3178 | |
| | .3010 | to change ½ g. to gram. |
| .4295 | 2.6567 | to change grams to pounds |
| | 3.3010 | to change pounds to tons |
| | − 2.1545 | |

14.3 mg. of radium per ton.

B — II is calculated in the same way. The standardization of this particular instrument was − 9.9825. The last four numbers are the same in the two cases. The number for the standardization of the instrument is the log of the number of grams of radium necessary to discharge the leaf one division per second. This is obtained by running through the instrument pitchblende or a radium solution the radium content of which is accurately known. In all cases the natural leak or a blank must be subtracted.

The instrument is charged 15 minutes before the readings are made in order to allow the active deposits of Radium A, B and C to collect on the wall of the chamber. The leaf system should be charged positively. The readings are taken at the end of three hours after the emanation is drawn into the chamber because the activity in-

creases to a maximum at that time. For the first part of the period the increase is very rapid. The maximum is actually reached at the end of four hours, but between three and five hours the change is very slow.

As soon as the readings are made the instruments must be freed from emanation by drawing dry air through them, the air being dried by sulphuric acid.

**II. Bisulphate Fusion.** — A pyrex test tube $1\frac{1}{8}$ in. in diameter and 8 in. long is filled about $\frac{1}{4}$ full of fused potassium bisulphate. Sodium bisulphate or a mixture of both potassium and sodium bisulphates may be used. From 0.05 to 5 grams of the finely ground sample should be added, the amount depending on the radium content of the

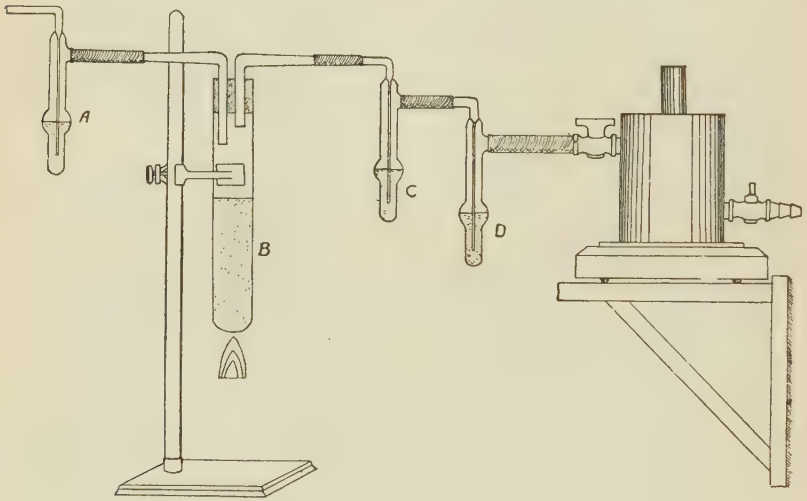



Fig. 101.

sample. Additional bisulphate is added until the tube is $\frac{3}{4}$ full. In adding the last bisulphate care should be taken to carry down any of the sample adhering on the side of the tube. The mixture is now thoroughly fused, continuing till reaction is complete. The test tube is removed from the flame and held in a nearly horizontal position and slowly turned while the melt solidifies. A very small amount of barium carbonate is dropped into the tube. About $\frac{1}{4}$ of a gram is sufficient. In cases of carnotite ores, slimes, and tails the fusion will be yellow. As soon as the tube is cool enough to be handled a rubber stopper carrying two outlet tubes drawn out to rather fine tips (see figure) is inserted. If this is done as soon as possible there will be a partial vacuum in the tube when it cools and this will indicate when the emanation is taken off that there has been no leak. One of the

outlet tubes should extend about one fourth way down the test tube and the other just through the stopper. After emanation has recovered at least one day the tube is connected to an evacuated chamber shown in Fig. 101. Micro-drying bulb *A* contains water or sulphuric acid and acts as an indicator to show when the current of air into the chamber is correctly regulated. *B* contains the fusion; *C* sodium hydroxide solution; *D* sulphuric acid. The tip near *A* is broken with a pair of pliers. On account of the vacuum in *B* air rushes through *A*. Immediately after breaking the first tip the second should be broken. The stopcock of the chamber is slowly opened till air bubbles rather slowly through *A*. The tube containing the fusion is carefully heated until all the fusion is melted. It is boiled for at least five

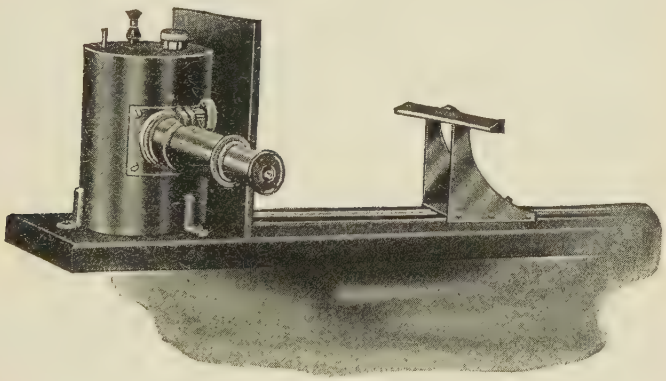


Fig. 102. Gamma Ray

minutes, or till the chamber is about to atmospheric pressure. During the heating, a steady current is maintained throughout the heating by regulating the stopcock of the chamber. The chamber is disconnected and set away to be read at the end of three hours. The procedure is the same from this point as in the carbonate fusion method.

## THE GAMMA RAY METHOD

The sample is placed in the holder at such a distance as will cause a reasonable rate of discharge — about one division per second. A standard is then placed at the same distance and the two rates of discharge compared. The natural leak should be subtracted from each reading. The quantities of radium are proportional to the rates of discharge.

In the gamma ray instrument the lead plate and the brass case of the chamber stop all the radiation except the gamma rays.

See Fig. 102.

### METHODS FOR SOLUTIONS

A measured volume of the solution is placed in a 150 cc. pyrex flask and dilute nitric acid added, filling the flask about one-half full. A little barium nitrate should be added to prevent the precipitation of radium sulphate. The solution is boiled to expel all the emanation. In the Colorado School of Mines a special flask with a long 1 in. neck is used. This is sealed off in the flame while the solution is nearly boiling. The ordinary flask may be used by inserting a rubber stopper carrying a tube which can be sealed. Or the neck of a pyrex flask can be drawn out and sealed. With the rubber stopper the emanation sometimes leaks. The special flasks are made by the Denver Fire Clay Company. After the emanation has recovered for one or more days the flask is connected to the burette by a light-walled rubber tube as in Fig. 99. The tip is broken and heat is applied to the flask. On breaking the tip the rubber tube collapses if the flask has not leaked. When the pressure in the tube is about atmospheric the stopcock is opened slightly from time to time until the gas goes into the burette, and then opened wide. The solution is boiled for about ten minutes. The gas is then drawn into an evacuated chamber, as described in the other methods. The calculation may be made in milligrams per liter.

NOTES. The carbonate method is similar to that given in bulletin 104, Bureau of Mines.

The bisulphate method of which the method here given is a modification was first published by Howard H. Barker in the Journal of Industrial and Engineering Chemistry for July, 1918, and improved by the Radium Company of Colorado.

Radium is found principally in carnotite and pitchblende. The largest carnotite deposits in the world are in southwestern Colorado and southeastern Utah. Uranium ores contain radium; the ratio of radium to that of uranium is $3.4 \times 10^{-7}$; or, there are 3.4 parts of radium to 10,000,000 of uranium.

Radium salts correspond chemically to those of barium. In water barium sulphate is 100 times as soluble as radium sulphate.

Radium is used in the treatment of certain malignant growths and in luminous paints. Some of the radioactive elements have furnished the means of studying atomic structure.

Emanation should not be allowed to remain in the chambers any longer than is necessary. Air dried by sulphuric acid should be drawn through them.[1]

[1] This chapter was contributed by Prof. L. D. Roberts, Associate Professor of Chemistry, Colorado School of Mines.

## RADIUM

TABLE OF RADIUM EMANATION RECOVERY (KOLOWRAT)

| $t$ | | Quantity Formed | Δ per hour | $t$ | | Quantity Formed | Δ per hour | $t$ | | Quantity Formed | Δ per hour |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Days | Hours | $1-e^{-\lambda t}$ | 0.00 | Days | Hours | $1-e^{-\lambda t}$ | 0.00 | Days | Hours | $1-e^{-\lambda t}$ | 0.00 |
| | 0 | 0.00000 | 747 | 2 | 4 | 0.32294 | 504 | 9 | 8 | 0.81363 | 1377 |
| | 1 | 0.00747 | 742 | 2 | 6 | 0.33302 | 496 | 9 | 12 | 0.81913 | 1326 |
| | 2 | 0.01489 | 736 | 2 | 8 | 0.34295 | 489 | 9 | 18 | 0.82709 | 1268 |
| | 3 | 0.02225 | 730 | 2 | 10 | 0.35274 | 482 | 10 | 0 | 0.83470 | 1212 |
| | 4 | 0.02955 | 726 | 2 | 12 | 0.36237 | 475 | 10 | 6 | 0.84197 | 1159 |
| | 5 | 0.03681 | 719 | 2 | 14 | 0.37187 | 468 | 10 | 12 | 0.84893 | 1108 |
| | 6 | 0.04400 | 715 | 2 | 16 | 0.38122 | 461 | 10 | 18 | 0.85558 | 1059 |
| | 7 | 0.05115 | 709 | 2 | 18 | 0.39043 | 454 | 11 | 0 | 0.86193 | 1013 |
| | 8 | 0.05824 | 703 | 2 | 20 | 0.39950 | 447 | 11 | 6 | 0.86801 | 0968 |
| | 9 | 0.06527 | 699 | 2 | 22 | 0.40844 | 440 | 11 | 12 | 0.87381 | 0925 |
| | 10 | 0.07226 | 693 | 3 | 0 | 0.41725 | 432 | 11 | 18 | 0.87937 | 0885 |
| | 11 | 0.07919 | 688 | 3 | 3 | 0.43022 | 422 | 12 | 0 | 0.88467 | 0846 |
| | 12 | 0.08607 | 683 | 3 | 6 | 0.44289 | 413 | 12 | 6 | 0.88975 | 0809 |
| | 13 | 0.09290 | 678 | 3 | 9 | 0.45529 | 404 | 12 | 12 | 0.89460 | 0775 |
| | 14 | 0.09968 | 672 | 3 | 12 | 0.46741 | 395 | 12 | 18 | 0.89924 | 0739 |
| | 15 | 0.10640 | 668 | 3 | 15 | 0.47926 | 386 | 13 | 0 | 0.90367 | 0701 |
| | 16 | 0.11308 | 663 | 3 | 18 | 0.49084 | 378 | 13 | 8 | 0.90928 | 0660 |
| | 17 | 0.11971 | 657 | 3 | 21 | 0.50217 | 369 | 13 | 16 | 0.91457 | 0622 |
| | 18 | 0.12628 | 653 | 4 | 0 | 0.51325 | 361 | 14 | 0 | 0.91954 | 0586 |
| | 19 | 0.13281 | 648 | 4 | 3 | 0.52408 | 353 | 14 | 8 | 0.92423 | 0552 |
| | 20 | 0.13929 | 643 | 4 | 6 | 0.53467 | 345 | 14 | 16 | 0.92864 | 0519 |
| | 21 | 0.14572 | 639 | 4 | 9 | 0.54502 | 337 | 15 | 0 | 0.93279 | 0489 |
| | 22 | 0.15211 | 633 | 4 | 12 | 0.55514 | 330 | 15 | 8 | 0.93671 | 0461 |
| | 23 | 0.15844 | 629 | 4 | 15 | 0.56504 | 323 | 15 | 16 | 0.94039 | 0434 |
| 1 | 0 | 0.16473 | 624 | 4 | 18 | 0.57472 | 315 | 16 | 0 | 0.94387 | 0409 |
| 1 | 1 | 0.17097 | 620 | 4 | 21 | 0.58418 | 308 | 16 | 8 | 0.94713 | 0385 |
| 1 | 2 | 0.17717 | 614 | 5 | 0 | 0.59343 | 3004 | 16 | 16 | 0.95021 | 0362 |
| 1 | 3 | 0.18331 | 611 | 5 | 4 | 0.60545 | 2915 | 17 | 0 | 0.95311 | 0341 |
| 1 | 4 | 0.18942 | 605 | 5 | 8 | 0.61711 | 2829 | 17 | 8 | 0.95584 | 0321 |
| 1 | 5 | 0.19547 | 601 | 5 | 12 | 0.62842 | 2745 | 17 | 16 | 0.95841 | 0303 |
| 1 | 6 | 0.20148 | 597 | 5 | 16 | 0.63941 | 2664 | 18 | 0 | 0.96084 | 0281 |
| 1 | 7 | 0.20745 | 592 | 5 | 20 | 0.65006 | 2585 | 18 | 12 | 0.96421 | 0257 |
| 1 | 8 | 0.21337 | 588 | 6 | 0 | 0.66040 | 2509 | 19 | 0 | 0.96729 | 0235 |
| 1 | 9 | 0.21925 | 583 | 6 | 4 | 0.67044 | 2435 | 19 | 12 | 0.97010 | 0214 |
| 1 | 10 | 0.22508 | 579 | 6 | 8 | 0.68018 | 2363 | 20 | 0 | 0.97268 | 0196 |
| 1 | 11 | 0.23087 | 575 | 6 | 12 | 0.68963 | 2293 | 20 | 12 | 0.97503 | 0179 |
| 1 | 12 | 0.23662 | 570 | 6 | 16 | 0.69881 | 2225 | 21 | 0 | 0.97718 | 0164 |
| 1 | 13 | 0.24232 | 567 | 6 | 20 | 0.70771 | 2160 | 21 | 12 | 0.97914 | 0150 |
| 1 | 14 | 0.24799 | 562 | 7 | 0 | 0.71635 | 2096 | 22 | 0 | 0.98094 | 0137 |
| 1 | 15 | 0.25361 | 557 | 7 | 4 | 0.72473 | 2034 | 22 | 12 | 0.98258 | 0125 |
| 1 | 16 | 0.25918 | 554 | 7 | 8 | 0.73286 | 1974 | 23 | 0 | 0.98408 | 0114 |
| 1 | 17 | 0.26472 | 549 | 7 | 12 | 0.74076 | 1915 | 23 | 12 | 0.98545 | 0104 |
| 1 | 18 | 0.27021 | 545 | 7 | 16 | 0.74842 | 1859 | 24 | 0 | 0.98670 | 0095 |
| 1 | 19 | 0.27566 | 542 | 7 | 20 | 0.75586 | 1804 | 24 | 12 | 0.98784 | 0087 |
| 1 | 20 | 0.28108 | 537 | 8 | 0 | 0.76307 | 1751 | 25 | 0 | 0.98889 | 0080 |
| 1 | 21 | 0.28645 | 533 | 8 | 4 | 0.77007 | 1699 | 25 | 12 | 0.98985 | 0073 |
| 1 | 22 | 0.29178 | 529 | 8 | 8 | 0.77687 | 1649 | 26 | 0 | 0.99072 | 0064 |
| 1 | 23 | 0.29707 | 525 | 8 | 12 | 0.78346 | 1600 | 27 | 0 | 0.99225 | 0053 |
| 2 | 0 | 0.30232 | 522 | 8 | 16 | 0.78986 | 1553 | 28 | 0 | 0.99353 | 0044 |
| 2 | 1 | 0.30754 | 517 | 8 | 20 | 0.79607 | 1507 | 29 | 0 | 0.99459 | 0037 |
| 2 | 2 | 0.31271 | 514 | 9 | 0 | 0.80210 | 1462 | 30 | 0 | 0.99548 | |
| 2 | 3 | 0.31785 | 509 | 9 | 4 | 0.80795 | 1419 | | | 1.00000 | |

Figures 98, 99 and 101 were drawn by M. Ettington.

## RHODIUM

**Element, Rhodium. Rh. at.wt. 102.9; sp.gr. 12.1; m.p. 1950° C.; oxides, RhO, $Rh_2O_3$, $RhO_2$.**

Rhodium is estimated mainly in ores, thermocouples and salts. *Minerals* see Platinum.

### DETECTION

Rhodium is found only in platinum ores. It is a white metal, difficultly fusible, and insoluble in acids. Rhodium, however, dissolves in aqua regia when alloyed with platinum, to a cherry-red solution. It is also soluble in molten phosphoric acid and dissolves when fused with acid potassium sulphate with the formation of $K_3Rh(SO_4)_3$. If the metal is treated with chlorine in the presence of sodium chloride there forms a soluble salt, $Na_3RhCl_6$.

Rhodium monoxide, RhO, is obtained by heating the hydroxide $Rh(OH)_3$, by cupellation of an alloy of rhodium and lead, or by igniting the finely-divided metal in a current of air. It is a grey powder with a metallic appearance, and is not attacked by acids, and when heated in hydrogen is reduced with evolution of light.

The oxide, $Rh_2O_3$, is obtained as a grey iridescent spongy mass by heating the nitrate. It is also formed as a crystalline mass when sodium rhodochloride is heated in oxygen. It is perfectly soluble in acids.

Rhodium dioxide, $RhO_2$, is obtained by repeated fusions of the metal with KOH and $KNO_3$. It is attacked neither by alkalies nor by acids and is reduced by hydrogen only at a high temperature.

**Hydrogen sulphide** precipitates from hot solution and incompletely a brown rhodium sulphide, $Rh_2S_3$. **Hydrogen** reduces rhodium salts.

**Potassium hydroxide** precipitates at first a yellow hydroxide, $Rh(OH)_3 + H_2O$ soluble in an excess of the reagent. If boiled, a gelatinous, dark-brown hydroxide, $Rh(OH)_3$, separates. A solution of $Na_3RhCl_6$ does not show this reaction immediately, but the precipitate appears in the course of time. Alcohol causes a black precipitate.

**Ammonium hydroxide** produces a yellow precipitate which is insoluble in HCl.

**Potassium nitrite** precipitates from hot solutions a bright yellow precipitate of double nitrite of potassium and rhodium.

**Zinc, iron and formic acid** precipitate rhodium as a black metal.

To detect small amounts of rhodium in the presence of other metals, evaporate the solution and displace with a fresh solution of sodium hypochlorite; the yellow precipitate formed is soluble after an addition of acetic acid. After a long agitation the solution changes to an orange-yellow color and after a short time the color passes and finally a grey precipitate settles and the solution turns sky-blue.

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

When rhodium is estimated in thermo couples or other alloys of platinum and rhodium the wire or sample is rolled to a thin ribbon and dissolved in aqua regia. Both metals will go into solution, forming the chlorides of rhodium and platinum. The aqua regia will have to be replaced from time to time, as the alloy dissolves slowly.

The rhodium from salts is precipitated with zinc and the black metallic rhodium cleaned with dilute aqua regia, filtered, washed, ignited and reduced with hydrogen.

Some alloys and ores are alloyed with silver and the silver and platinum are dissolved in $HNO_3$. The residue is cleaned with aqua regia, dried, and weighed as metallic rhodium. If the residue is ignited reduce with hydrogen.

The material or residue containing rhodium is fused with $KHSO_4$ for some time at a low red heat and the mass leached with hot water acidified with HCl. The rose-red solution contains the rhodium.

**Separation of Rhodium from Platinum.** — Alloys and ores containing platinum and rhodium dissolve slowly in aqua regia as stated above. After expelling the $HNO_3$ add $NH_4Cl$. The precipitate is filtered and washed with dilute ammonium chloride solution, which dissolves the rhodium salt. A very small amount of rhodium will color the filtrate pink to a rose-red color, depending on the amount of rhodium present.

**Separation of Rhodium from Iridium.** — See Separation of Rh from Pt.

A separation can be made by adding sodium nitrite in excess to the solution of the two metals, with a sufficient quantity of sodium carbonate to make the solution neutral or alkaline; this is boiled until the solution assumes a clear orange color. The rhodium and iridium are converted into soluble double nitrites. A solution of sodium sulphide is added in slight excess and the liquid made slightly acid. The rhodium is precipitated as dark-brown rhodium sulphide.

A solution of rhodium and iridium is evaporated with HCl and displaced with a large excess of acid sodium sulphite, $NaHSO_3$, and allowed to stand some time when a pale yellow double salt of rhodium and sodium sulphite slowly separates out while the solution becomes nearly colorless. Wash out the precipitate, and heat with hot concentrated $H_2SO_4$ till the sulphurous acid is driven off. Heat the material in a crucible until rid of all free sulphuric acid. Then the iridium is dissolved out as a sulphate with a deep chrome green color, while a double salt of sodium sulphate and rhodium oxide remains behind. This is flesh color, insoluble in water and acids. Boil with aqua regia, wash, dry, heat and it decomposes into rhodium and sodium sulphate.

Rhodium can also be separated from iridium, when the latter is present as an iridic salt such as $Ir(SO_4)_2$, by precipitating the mixed salts with caustic potash, dissolving the hydroxides in dilute sulphuric acid and adding caesium sulphate. The sparingly soluble rhodium caesium-alum separates in the cold, and can readily be purified by recrystallization and then by electrolysis.

**Separation of Rhodium, Platinum and Palladium.** — Having the three in solution precipitate the platinum with $NH_4Cl$ as described under Platinum. After filtering off the $(NH_4)_2PtCl_6$ precipitate, and after neutralizing the filtrate with $Na_2CO_3$ add mercuric cyanide to separate the palladium as $Pd(CN)_2$ as described under palladium. The filtered solution is evaporated to dryness with an excess of HCl. On treating the residue with alcohol, the double chloride of rhodium and sodium is left undissolved as a red powder. By heating this in a tube through which hydrogen is passed the rhodium is reduced to the metallic state and the sodium chloride is washed out with water leaving a grey powder of metallic rhodium.

**Separation of Rhodium from Ruthenium.** — The solution containing the two metals is treated with sodium nitrite as above and evaporated to dryness. The residue is powdered and treated in a flask with absolute alcohol. After filtering and washing with alcohol the rhodium remains undissolved.

The substance or residue containing the rhodium and ruthenium may be fused with $KHSO_4$ in a porcelain or platinum crucible causing the rhodium to go into solution as already described. The ruthenium remains insoluble.

## GRAVIMETRIC METHOD FOR THE DETERMINATION OF RHODIUM

The solution containing rhodium is treated with zinc and the residue is washed well with hot water acidulated with HCl. The residue is then cleaned with dilute aqua regia and the black metallic rhodium is filtered off, dried, and ignited in hydrogen. Cool and weigh as metallic rhodium.

The metals may be melted with lead or silver and the buttons dissolved in dilute $HNO_3$, leaving a residue which is treated with dilute aqua regia to dissolve any platinum that might be present. The residue is treated with salt and chlorine and the melt dissolved in water as described under Iridium. The iridium is precipitated with $NH_4Cl$ and the rhodium with zinc. The rhodium black is cleaned with dilute aqua regia, filtered, washed and ignited. Reduce in hydrogen and weigh as metallic rhodium.

The solution containing the rhodium is made alkaline with KOH and then acid with formic acid. Boil, and the rhodium will be precipitated as finely divided metallic rhodium. After filtering proceed in the usual manner.[1]

[1] Chapter contributed by R. E. Hickman.

## RUTHENIUM

**Element, Ruthenium. Ru. at.wt. 101.7; sp.gr. 12; m.p. 2450° C.? oxides, $Ru_2O_3$, $RuO_2$, $RuO_4$.**

Ruthenium is generally estimated in alloys, ores and residues. *Minerals* see Platinum.

### DETECTION

This element is found only in platinum ores. It is barely soluble in aqua regia, and insoluble in acid potassium sulphate. It dissolves when fused with KOH and $KNO_3$. The solution of the fusion when dissolved in water forms potassium ruthenate, $K_2RuO_4$, from which $HNO_3$ precipitates the hydroxide, which is soluble in HCl. The treatment with chlorine and KCl at a high temperature yields a salt of $K_2RuCl_6$. The salts that are most common are $K_2RuCl_5$ and $K_2RuCl_6$.

The oxide, $Ru_2O_3$, is formed when finely divided ruthenium is heated in the air, forming a blue powder which is insoluble in acids. It can also be obtained by heating the trihydroxide, $Ru(OH)_3$, in dry carbon dioxide which forms a black, scaly mass.

Ruthenium dioxide, $RuO_2$, is obtained by roasting the disulphide or sulphate in contact with air. It is likewise formed when the metal is fused in an oxidizing atmosphere, when it burns with a sparkling smoky flame, and evolves an ozone-like smell.

Ruthenium tetroxide, $RuO_4$, is formed in small quantities when the metal is heated at 1000° C in a current of oxygen, although when heated alone it decomposes at about 106°. It is prepared by passing chlorine into a solution of potassium nitrosochlororuthenate, or of potassium ruthenate or sodium ruthenate prepared by fusing the metal with sodium peroxide; the liquid becomes heated and the tetroxide distills over and is deposited in the receiver. The moist oxide quickly decomposes. In the dry state it is fairly stable, but decomposes in sunlight with the formation of lower oxides. It dissolves slowly in water, and the solution when it contains free chlorine or HCl may be kept without alteration for some days if light be excluded, but when pure slowly deposits a black precipitate.

In addition to the above oxides, salts corresponding to the acidic oxides $RuO_3$ and $Ru_2O_7$ have been prepared.

**Potassium hydroxide** precipitates a black hydroxide easily soluble in HCl.

**Hydrogen sulphide** slowly produces brown $Ru_2S_3$.

**Ammonium sulphide** precipitates brownish black sulphide.

**Metallic zinc** precipitates metallic ruthenium, the solution first turning blue.

**Potassium sulphocyanate** gives on heating a dark brown solution.

**Silver nitrate** gives a rose-red precipitate.

**Mercurous nitrate** produces a bright blue precipitate.

**Zinc chloride** produces a bright yellow precipitate which darkens on standing.

**Potassium iodide** after a time by heating precipitates the black sesqui-iodide.

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

When ruthenium is alloyed with platinum or gold, aqua regia dissolves these metals, forming the chlorides of platinum, gold and ruthenium. The ruthenium in ores is in the form of an alloy with platinum or osmiridium. This is fused with $KNO_3$ and KOH in a silver crucible, the osmium and the ruthenium forming salts as described above, while the iridium remains as an oxide.

**Separation of Ruthenium from Platinum.** — The two metals are precipitated with KCl and the potassium rutheniochloride is dissolved out with cold water containing a very small amount of KCl and alcohol. The ruthenium is then precipitated from an acid solution by additions of granulated zinc.

A separation may be made by alloying with silver and dissolving the platinum and silver by $HNO_3$, the ruthenium remaining as the residue.

From a concentrated solution of these metals precipitate the platinum with $NH_4Cl$. Evaporate the filtrate with potassium nitrate to dryness and boil the residue with alcohol when the residual platinum will remain behind and the ruthenium goes into solution.

**Separation of Ruthenium from Iridium.** — The two metals are fused with KOH and $KNO_3$ as described above, the ruthenium forming a salt soluble in water and the iridium remaining as an oxide.

To the solution of the two metals, sodium nitrite is added in excess, with sufficient sodium carbonate to keep the liquid neutral or alkaline. The whole is boiled until an orange color appears. The ruthenium and the iridium are converted into soluble double nitrites. Sodium sulphide is then added, small quantities at a time until the precipitated ruthenium sulphide is dissolved in the excess of alkaline sulphide. At first the addition of the sulphide gives the characteristic crimson tint due to ruthenium, but this quickly disappears and gives a bright chocolate-colored precipitate. The solution is boiled for a few minutes, and allowed to become perfectly cold and then dilute HCl cautiously added until the dissolved ruthenium sulphide is precipitated and the solution is faintly acid. The solution is filtered and the precipitate washed with hot water. The filtrate will be free from ruthenium.

The fusion with KOH and $KNO_3$ as described above is dissolved in water in a flask or retort; chlorine is passed through this solution and thence into two or three flasks containing a solution of KOH and alcohol. The two or three flasks which form the condensing apparatus should be kept as cold as possible. The ruthenium is transformed into volatile $RuO_4$ which condenses in the flasks, while the iridium remains in the retort.

**Separation of Ruthenium from Rhodium.** The mixed solution of the two metals is treated with potassium nitrite as described above. The orange-yellow solution is evaporated to dryness upon the water bath and treated with absolute alcohol. The rhodium remains undissolved and can be filtered off and washed with alcohol. The rhodium salt can be ignited with $NH_4Cl$ and after washing yields metallic rhodium. See Separation of Rhodium from Ruthenium.

**Separation of Ruthenium from Osmium.** — See Separation of Osmium from Ruthenium.

## GRAVIMETRIC METHOD FOR THE DETERMINATION OF RUTHENIUM

Ruthenium is best weighed as the residue, or metallic ruthenium, after the other metals are eliminated. It may be precipitated from the solution with zinc and after filtering, washing and igniting the filter the impurities are dissolved in dilute aqua regia; reduce in hydrogen and the residue is ruthenium. The platinum metals may be alloyed with silver and after dissolving out the silver, platinum and palladium with $HNO_3$, the residue is treated with dilute aqua regia as above, leaving the residue as ruthenium. If iridium is present in the residue, weigh as iridium and ruthenium. Make a fusion with KOH and $KNO_3$ as described under iridium; dissolve the fusion and filter off the $Ir_2O_3$, and wash with sodium hypochlorite solution and then with water. Ignite and weigh as $Ir_2O_3$. Calculate the weight of Ir which is to be subtracted from the weight of the ruthenium and iridium. The difference is ruthenium. If rhodium is present fuse with $KHSO_4$ as described under rhodium.

The solution of $Ru_2Cl_6$ is evaporated to drive off the excess acid and then taken up with 50 to 60 cc. of water and a few pieces of magnesium added gradually. The solution is filtered and the residue washed with a 5% $H_2SO_4$ solution to get rid of any magnesium that may be present. Ignite at the lowest possible temperature, and heat in hydrogen to red heat, cool and weigh as metallic ruthenium.[1]

[1] Chapter contributed by R. E. Hickman

## SELENIUM AND TELLURIUM

**$Se_8$, at.wt. 79.2; sp.gr. { amorphous 4.26; m.p. 217°; / crystalline 4.82; } b.p. 690° C.; oxide $SeO_2$; acids, $H_2SeO_3$, $H_2SeO_4$.**

**Te, at.wt. 127.5; sp.gr. 6.27; m.p. 452°; b.p. 1390° C.; oxides TeO, $TeO_2$, $TeO_3$; acids, $H_2TeO_3$, $H_2TeO_4$.**

### OCCURRENCE

Selenium and tellurium closely resemble sulphur in chemical properties. They have crystalline and amorphous forms. The elements occur in nature frequently associated with sulphur. Selenium is frequently present in iron pyrites, hence is found in the flue dust of lead chambers of the sulphuric acid plant, and as an impurity in sulphuric acid, prepared from pyrites containing selenium.

**Ores — Selenium.** — In copper and iron pyrites; meteoric iron. In the rare minerals *clausthalite*, PbSe; *lehrbachite*, PbSe.HgSe; *onofrite*, HgSe.4HgS; *eucairite*, $Cu_2Se.Ag_2Se$; *crookesite*, $(CuTlAg)_2Se$.

**Tellurium.** — Occurs in tellurides and arsenical iron pyrites. Frequently associated with gold, silver, lead, bismuth and iron. In the minerals — *altaite*, PbTe; *calaverite*, $AuTe_2$; *coloradolite*, HgTe; *nagyagite*, $(AuPb)_2(TeSSb)_3$; *petzite*, $(Ag\text{-}Au)_2Te$; *sylvanite*, $(AuAg)Te_2$; *tellurite*, $TeO_2$ (tellurium ochre); *tetradymite*, $Bi_2(Te,S)_3$.

### DETECTION

Selenium and tellurium appear with the hydrogen sulphide subgroup elements in the ordinary course of qualitative analysis. The acid solution of the material is treated cold with $H_2S$, as the lemon-yellow SeS formed in a cold solution is more readily soluble in alkaline sulphide solutions than the orange-yellow $SeS_2$ precipitated from hot solutions. Although only a partial separation takes place the extract will contain sufficient selenium, if present in the sample, to give a qualitative test. By precipitation from an acid solution by $H_2S$, selenium and tellurium are separated from members of subsequent groups. The sulphides precipitated are extracted with sodium or ammonium sulphide and the extract examined for selenium and tellurium.

### Detection of Selenium

The sodium or ammonium extract is acidified with hydrochloric acid, whereby selenium together with the other members of the group are precipitated. The washed and dried precipitate is mixed with twice its weight of a flux containing equal parts of sodium carbonate and nitrate, and the mixture added to an equal amount of the flux which has been previously fused. The fluid mass is poured on to a slab of porcelain and the cooled melt placed in a beaker and extracted with water, whereby selenic, telluric, molybdic and arsenic acids dissolve, stannic oxide, sodium antimonate, gold and the platinum group remaining insoluble. The extract is treated with an excess of hydrochloric acid and boiled to reduce sodium selenate, $Na_2SeO_4$, to selenious acid, $H_2SeO_3$. A reducing agent such as sulphurous acid, ammonium sulphite, hydrazine sulphate or hydroxylamine is added and the solution boiled. Selenium, if present, is precipitated in its red or brown-colored metallic form. The red color darkens on boiling.

Selenium is an odorless and tasteless solid. *Its vapor* has a putrid horseradish odor. The element burns with a reddish-blue colored flame.

Dissolved in *concentrated sulphuric acid* a fine green-colored solution is obtained, from which solution selenium may be precipitated by dilution with water, the suspended substance giving a reddish tint to the acid.

**Hydrochloric acid** decomposes selenates with evolution of chlorine gas on boiling.

**Barium chloride** precipitates white $BaSeO_3$, soluble in dilute HCl, when added to selenites, and white $BaSeO_4$, insoluble in dilute HCl, when added to selenates.

**Hydrogen sulphide** produces no precipitate with a selenate. This reduced, however, by heating with HCl, a lemon-yellow to orange-yellow precipitate of $SeS_2$ is obtained.

The gas passed into a solution of selenite gives an immediate precipitation of the sulphide, $SeS_2$.

### Detection of Tellurium

Tellurium dissolved in *concentrated sulphuric acid* colors the acid purple or carmine. The color disappears on dilution. The mineral may be treated directly with hot concentrated sulphuric acid and the color obtained in presence of tellurium.

**Heated** in a test-tube tellurium compounds sublime and fuse to colorless, transparent drops of $TeO_2$.

**Hydrogen sulphide** precipitates metallic tellurium mixed with sulphur when passed into acid solutions containing the element. The precipitate resembles SnS in appearance. It is readily soluble in $(NH_4)_2S$.

Tellurium *burns* with a greenish flame.

**Reducing agents** added to acid solutions of tellurium precipitate black metallic tellurium.

Tellurium compounds are not as readily reduced as are those of selenium. In solutions having an acidity of over 80 per cent, $SO_2$ gas causes the precipitation of metallic selenium alone. Upon dilution with an equal volume of water tellurium is precipitated. A separation may be effected in this way.

Tellurates *boiled with HCl* evolve chlorine gas and are reduced to $H_2TeO_3$. Dilution of the solution will cause the precipitation of $TeO_2$ (distinction from Se).

**Potassium iodide** added to a tellurite in dilute sulphuric acid solution (1 : 4) precipitates black $TeI_4$, soluble in excess of KI.

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

The following facts regarding solubilities of these elements and their compounds may be useful in the analysis of these substances.

**Selenium.** — Amorphous selenium is soluble in carbon disulphide; the crystalline hexagonal form is insoluble in this reagent. The metal is soluble in hydrochloric acid in the presence of nitric acid. It is soluble in cold concentrated sulphuric acid, giving a green-colored liquid, which diluted with water deposits selenium. The dioxide, $SeO_2$, is readily soluble in hot water.

**Tellurium.** — The element dissolves in hot concentrated hydrochloric acid. On dilution of the solution a precipitation of $H_2TeO_3$. $TeO_2$ occurs. Treated with concentrated nitric acid or aqua regia $H_2TeO_4$ forms. With sulphuric acid the compound $H_2TeO_3$ forms and $SO_2$ is evolved. The element dissolves in concentrated potassium cyanide, from which solution hydrochloric acid precipitates all of the tellurium. Tellurium is insoluble in carbon disulphide. The oxides TeO and $TeO_2$ are soluble in acids, $TeO_3$ being not readily soluble. All the oxides dissolve in hot potassium hydroxide solutions.

Care must be exercised to avoid overheating acid extracts in the preparation of the sample, since loss by volatilization is apt to occur; this is especially true of the halogen compounds of selenium and tellurium, the former being more volatile than the latter. (B.p. $SeCl_2$ = 145°; $SeBr_2$ = 225° – 230°; $SeOCl_2$ = 179.5°; $TeCl_2$ = 327°; $TeCl_4$ = 414°; $TeBr_2$ = 339°; $TeBr_4$ = 420° C.) [1]

**Fusion Method.** — The finely powdered substance is intimately mixed with about five times its weight of a flux of sodium carbonate and nitrate (4 : 1) and heated gently in a nickel crucible, gradually increasing the heat, until the charge has fused. When the molten mass appears homogeneous, it is cooled and extracted with water. Sodium selenate and tellurate pass into solution and are separated from most of the heavy metals. The water extract is acidified with hydrochloric acid and boiled until no more free chlorine is evolved. (Test with starch iodide paper. Cl = blue color.) Metallic selenium and tellurium may be precipitated by passing sulphur dioxide into the hydrochloric acid solution.

Keller has shown that tellurium is not precipitated by $SO_2$ in strong hydrochloric acid solutions (sp.gr. 1.175), whereas selenium is precipitated. Diluted with an equal volume of water (acidity 30 to 50% of above) both tellurium and selenium are precipitated by $SO_2$.

One or more of the following procedures may be required according to the material that is being analyzed.

**Separation of Selenium and Tellurium from the Iron and Zinc Groups, from the Alkaline Earths and the Alkalies.** — If sulphur dioxide is passed into a solution containing 30 to 50% of hydrochloric acid

(sp.gr. 1.175), selenium and tellurium will be precipitated, the other elements remaining in solution. If the acidity is over 80% of the above strength of hydrochloric acid, only selenium is precipitated.

The presence of nitric and of sulphuric acid prevents the complete precipitation of tellurium.

**Separation of Selenuim and Tellurium from Cadmium, Copper and Bismuth.** — Sulphur dioxide passed into an acid solution containing 30 to 50% of hydrochloric acid (sp.gr. 1.175) precipitates selenium and tellurium free from cadmium, and the greater part of bismuth, copper, antimony, etc. Complete separation of selenium and tellurium may be effected by the distillation process described under Separation of Selenium and Tellurium, see below.

**Separation from Silver.** — Silver is precipitated as the chloride AgCl, selenium and tellurium remaining in solution.

**Separation from Gold.** — The slightly acid solution, free from nitric acid, is diluted with water, ammonium oxalate or oxalic acid added and the precipitated gold allowed to settle several hours (preferably twenty-four hours or more). The gold is filtered off and the selenium and tellurium precipitated in the filtrate with sulphur dioxide.

In the absence of selenium, gold may be separated from tellurium by precipitation with ferrous sulphate added to the solution strongly acidified with hydrochloric acid. Tellurium remains in solution. (Selenium is also precipitated with ferrous sulphate.)

**Separation of Selenium from Tellurium in Strong Hydrochloric Acid by Direct Precipitation with Sulphur Dioxide — Keller's Method.** — The procedure has already been mentioned. Advantage is taken of the fact that tellurium is not precipitated by $SO_2$ in strong hydrochloric acid solutions, whereas selenium is precipitated.

**Procedure.** — The two elements are precipitated by sulphur dioxide from an acid solution containing 30 to 40% of strong hydrochloric acid. The precipitate is dissolved in nitric acid and the solution evaporated to dryness on the steam plate. The residue is treated with 200 cc. of hydrochloric acid (sp.gr. 1.175) and boiled to free the solution of nitric acid, since the presence of this acid prevents complete precipitation of tellurium. A little sodium chloride is previously added to minimize the loss through volatilization during the heating. The hot solution is saturated with sulphur dioxide, whereupon selenium is quantitatively precipitated and may be filtered off, washed with a 90% solution of strong hydrochloric acid (sp.gr. 1.175, i.e., 9 parts of HCl to 1 part by volume of $H_2O$), followed by dilute acid, then by water until free of acid, and finally by alcohol. Weigh as metallic selenium after drying at 105° C. The tellurium is precipitated from the filtrate by diluting this with an equal volume of water, heating to boiling and again saturating with sulphur dioxide. The precipitate is washed with dilute hydrochloric acid (1 : 1), followed by water and alcohol, then dried and weighed as tellurium.

## GRAVIMETRIC METHODS FOR DETERMINING SELENIUM AND TELLURIUM

The sections on Preparation and Solution of the Sample and Separations should be carefully studied, as details for the precipitation of selenium and tellurium are given.

### SELENIUM

#### Precipitation of Selenium by Sulphur Dioxide

**Procedure.** — The sample obtained in solution according to the procedure outlined under Preparation and Solution of the Sample and freed from nitric acid, is saturated with sulphur dioxide, whereupon selenium is precipitated in its elemental condition. If the solution is strongly acid with hydrochloric acid (HCl = sp.gr. 1.175), tellurium remains in solution, if present. It is advisable to wash the precipitated selenium with moderately strong hydrochloric acid, followed by the dilute acid, then with water until free of acid, and finally with alcohol. The residue is dried at 105° C. and weighed as metallic selenium.

The filtrate should be tested for selenium by saturating again with $SO_2$. Tellurium precipitates quantitatively from hydrochloric acid solution of half the above strength, hence will be evident in the filtrate, if present.

$$\frac{\text{Weight of Se} \times 100}{0.5} = \% \text{ Se.}$$

#### Reduction to Metallic Selenium Potassium Iodide Method

The method worked out by Peirce is useful in determining selenium in samples containing less than 0.1 gram of selenium. Larger amounts are apt to occlude iodine, giving high results.

**Procedure.** — The sample containing selenious acid or a selenite is diluted to 400 cc. and acidified with hydrochloric acid. Potassium iodide is added in excess, about 3 grams more than is required to effect reduction, and the solution boiled about twenty minutes. The precipitate is filtered and washed as usual, then dried and weighed as metallic selenium.

## TELLURIUM

Consult procedure under separation of selenium and tellurium then proceed further as follows:

**Determination of Tellurium.** — The residue in the distilling flask is transferred to a 600 cc. beaker containing 150 cc. of cold water. Ten cc. of 3% $Fe(NO_3)_3$ solution is added, made ammoniacal, and then heated to boiling; the precipitate is filtered off on a large filter and washed with hot water. The precipitate is dissolved in hot dilute HCl and the solution nearly neutralized with $NH_4OH$. The slightly acid solution is saturated with $H_2S$, the precipitated tellurium filtered off on a 12½ cm. filter, and washed with $H_2S$ water.

The precipitate is dissolved off the paper into a small beaker with a mixture of equal parts of HCl and bromine-potassium bromide solution. The paper is washed with water keeping the volume of the solution as small as possible. The filtrate should contain 20% HCl.

Tellurium is precipitated by saturating the solution with $SO_2$. The precipitate, after heating to boiling, is allowed to settle for several hours and filtered on a weighed Gooch. It is washed with hot water and then with alcohol and dried for an hour at 100° C., cooled in a desiccator and weighed.

$$\frac{\text{Weight of Te} \times 100}{0.5} = \% \text{ Te.}$$

### Determination of Tellurium where Selenium is not Desired

**Procedure.** — A sample of 1 to 5 grams is taken for analysis and placed in a No. 5 porcelain crucible. Ten cc. of conc. $HNO_3$ are added very cautiously and, when the apparent action has ceased, the sample is placed on the steam bath until all $NO_2$ fumes have been expelled. Four to 5 drops of conc. $H_2SO_4$ are now added and the solution evaporated to dryness on the steam bath. About 15 cc. of conc. HCl are added and the solution again evaporated to dryness. By this latter procedure any selenium that may be present is converted to the easily volatile chloride. The crucible is placed on a triangle on a wire gauze over a low flame and heated cautiously until all white fumes have disappeared and then at dull red heat until all signs of crystallized selenious chloride have disappeared. The residue in the crucible is tellurious dioxide and ferric oxide.

The crucible is cooled and the residue dissolved in conc. HCl in a No. 4 beaker and the solution diluted to 250 cc. with distilled water. $H_2S$ is passed into the solution until tellurium is completely precipitated. The precipitate is filtered on a 12½ cm. filter, and washed with $H_2S$ water.

The precipitate is dissolved in a 250 cc. beaker by adding a mixture of bromine-potassium bromide (200 cc. of liquid bromine added to 320 grams of KBr salt that has been dissolved in just sufficient water to form a saturated solution), 1 part and conc. HCl, 1 part, using the least amount of the mixture necessary to dissolve the precipitate and wash with a little water. The filtrate should contain 20% of HCl.

The solution is thoroughly saturated with $SO_2$ gas, and then heated to boiling. The precipitated tellurium is allowed to settle for several hours, preferably over night, and filtered on a weighed Gooch crucible, then washed with hot water and finally with alcohol. After drying for an hour at 100° C., the tellurium is cooled and weighed.

Weight of the residue multiplied by 100 divided by weight taken gives per cent tellurium.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Commercial Selenium

**Selenium.** — Weigh out four one-half gram (.5000 g.) portions of the finely ground sample (100 mesh) into a 150 cc. beaker. Add 10 cc. of $H_2O$, then add slowly 15 cc. of conc. $HNO_3$ and cover with a watch glass.

Evaporate to dryness on the water bath,[1] take up with 10 cc. of HCl (1:1) and 20 cc. of $H_2O$ in the cold. Filter off the insoluble into a 400 cc. beaker; to the filtrate add sufficient conc. HCl to make a solution of 70% conc. HCl by volume.

Precipitate the selenium at room temperature by a slow current of $SO_2$ gas at the rate of two small bubbles a second, stirring frequently to granulate the selenium. Care must be taken to keep the solution at room temperature, 60–70° F., by placing the beaker in a vessel of running tap water.[2]

When all the selenium has been precipitated and the solution smells strongly of $SO_2$, remove and allow to settle for one-half hour.

Decant the supernatant liquor through a tared Gooch crucible and wash the precipitated selenium in the beaker three times with conc. HCl and once with cold water, decanting each time through the crucible.

Add to the precipitate still in the beaker 25 cc. of cold water and from a wash bottle an ordinary stream of hot water with vigorous

[1] Evaporating to dryness on a hot stove in place of the water bath, causes a loss of selenium by volatilization.

The author claims there is an appreciable loss of selenium when heated above 105° C. and of selenium in the form of chloride when heated above 100° C., even in the presence of sodium and potassium chlorides.

[2] If the temperature of the solution when precipitating selenium is above 70° F., the selenium balls up, occluding impurities which can never be washed out; if below 60° F., incomplete precipitation occurs.

stirring, until the selenium turns black and granular.[1] The selenium is then readily filtered off, washed with hot water, finally with alcohol and dried at 105° C. to constant weight. Weigh as metallic selenium.

In order to quickly obtain a constant weight, it is sometimes necessary to break up the precipitate of the selenium in the crucible with a platinum rod to facilitate the driving off of the moisture.

After the final weight is obtained, the crucible is gently heated, to expel the selenium. This is a check on the weight and the purity of the precipitated selenium.[2]

## TELLURIUM

Add three (3) grams of powdered tartaric acid to the filtrate from the selenium precipitate, dilute to four times its bulk with hot water, then add 25 cc. of $NH_4OH$. Saturate the liquid with $SO_2$ gas (takes about two minutes) and bring to a boil. Allow to stand for two hours, or longer, on a hot plate. The granular precipitate is filtered on a tared Gooch crucible, washed with hot water, dried at 115° C. to constant weight and weighed as metallic tellurium.

[1] If the precipitated selenium is not made granular as above, it cakes in drying and holds moisture even at 110° C. If the water is too hot the selenium partially melts; if too cold, it does not accomplish the purpose. A temperature of 70° C. is about right. A little experience will accomplish the correct results.

[2] The residue may consist of silica and gold.

## SILICON

**Si, at. wt. 28.3; sp.gr. amor. 2.00.; crys. 2.49; m.p. 1420° C.; oxides SiO, $SiO_2$**

The element silicon has no important application. Its use for electrical resistance has been suggested. A rod 10 cm. long with cross section of 40 sq.mm. has a resistance of 200 ohms against a carbon rod of the same dimensions of 0.15 ohm. Impure silica finds use in fluxes in manufacture of glass; pure silica for the manufacture of silica ware. With caustic it forms an adherent sodium silicate. Silicon carbide, carborundum, is used for refractory purposes, fire brick, zinc muffles, coke ovens. Crystolon, the crystalline form, is used as an abrasive, in making grinding wheels, sharpening stones, etc.

Combined as $SiO_2$ and in silicates the element is very widely distributed in nature and is a required constituent in practically every complete analysis of ores, minerals, soils, etc. It is present in certain alloys, ferro-silicon, silicon carbide, etc.

### Minerals of Silica

### Silicates Undecomposed by Acids

*Amphibole* group — Actinolite, $Ca(Mg,Fe)_3(SiO_3)_2$; *Hornblend*, chiefly $Ca(Mg,Fe)_3(SiO_3)_4$ with $Na_2Al_2(SiO_3)_4$ and $(Mg,Fe)_2(Al,Fe)_4SiO_{12}$; *Tremolite*, $CaMg_3(SiO_3)_4$. *Andalusite*, $(AlO)AlSiO_4$. *Beryl*, $Be_3Al_2(SiO_3)_6$. *Cyanite*, $Al_2SiO_5$. *Epidote*, $Ca_2(FeOH)Fe_2(SiO_4)_3$. Al may replace Fe. *Feldspar* group — *Albite*, $NaAlSi_3O_8$; *Andesine*, Silicate of Na, Al and Ca; *Celsian*, $BaAl_2Si_2O_8$; *Microcline*, $KAlSi_3O_8$; *Oligoclase*, $NaAlSi_3O_8.CaAl_2Si_2O_8$; *Orthoclase*, $KAlSi_3O_8$. *Garnet* group, silicates of Ca, Mg, Fe, Mn, Al, Cr, Ti. *Kaolinite*, $2H_2O.Al_2O_3.2SiO_2$; *Halloysite*, amorphous variety. *Pyroxene* group — *Acmite*, $Na_2O.Fe_2O_3.4SiO_2$; *Augite*, $CaMgSi_2O_6$; *Diopside*, $CaMg(SiO_3)_2$; *Enstatite*, $MgSiO_3$; *Hypersthane*, $(Fe,Mg)SiO_2$; *Rhodonite*, $MnSiO_3$. *Spondumene*, $LiAl(SiO_3)_2$. *Staurolite*, $H_2O.2FeO.5Al_2O_3.4SiO_2$. *Tale*, $H_2O.3MgO.4SiO_2$. *Titanite*, $CaTiSiO_5$ (sol. in $H_2SO_4$). *Tapaz* $[Al(F,OH)_2]AlSiO_4$. *Tourmaline*, $H_9Al_3(B.OH)_2Si_4O_{19}$. H may be replaced by K, Na, Mg, Ca and Fe.

### Silicates Decomposed by Acids

*Anorthite*, $CaAl_2Si_2O_8$; *Calamine*, $H_2O.2ZnO.SiO_2$; *Chrysocolla*, $CuSiO_3.2H_2O$; *Chrysolite* or *Olivine*, $(Mg,Fe)_2SiO_4$; *Datolite*, $HCaBSiO_5$; *Garnierite*, $H_2(Ni,Mg)SiO_4$ + Aqua; *Leusite*, $KAl(SiO_3)_2$; *Natrolite*, $Na_2Al_2Si_3O_{10}.2H_2O$; *Nephelite*, $K_2Na_6Al_8Si_9O_{34}$; *Prehemite*, $H_2Ca_2Al_2$

$(SiO_4)_3$; *Serpentine*, $3MgO.2SiO_2.2H_2O$; *Vesuvianite*, basic CaAl silicate; *Wernerite*, silicate of Ca, Al, Na with Cl; *Willemite*, $Zn_2SiO_4$; *Wollastonite*, $CaSiO_3$; *Zeolite group*, hydrous silicates.

### DETECTION

The finely ground sample together with a small quantity of powdered calcium fluoride is placed in a small lead cup, 1 cm, in diameter and depth (see Fig. 103), and a few drops of concentrated sulphuric acid added. A lead cover, with a small aperture, is placed on the cup, and the opening covered with a piece of moistened black filter paper. Upon this paper is placed a moistened pad of ordinary filter paper. The cup is now gently heated on the steam bath. At the end of about ten minutes a white deposit will be found on the under side of the black paper, at the opening in the cover, if an appreciable amount of silicon is present in the material tested.

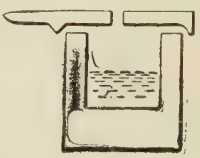


Fig. 103

A silicate, fused with sodium carbonate or bicarbonate in a platinum dish and the carbonate decomposed by addition of hydrochloric acid with subsequent evaporation to dryness, will liberate silicon as silicic anhydride, $SiO_2$. The silica placed in a platinum dish is volatilized by addition of hydrofluoric acid, the gaseous silicon fluoride being formed. A drop of water placed in a platinum loop, held in the fumes of $SiF_4$, will become cloudy owing to the formation of gelatinous silicic acid and fluosilicic acid,

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6.$$

If a silicate is fused in a platinum loop with microcosmic salt, the silica floats around in the bead, producing an opaque bead with web-like structure upon cooling.

## METHODS OF ANALYSIS

**Preparation and Solution of the Sample.** — The gravimetric procedure is the only satisfactory method for the estimation of silicon. The substance in which the element is combined as an oxide or as a silicate is decomposed by acid treatment or by fusion with an alkali carbonate or bicarbonate, the material taken to dryness with addition of hydrochloric acid, whereby the compound silica is liberated. If other elements are present the silicon is volatilized by addition of hydrofluoric acid and estimated by the loss of weight of the residue.

The element is scarcely attacked by single acids, but is acted upon by nitric-hydrofluoric acid mixture. It dissolves in strong alkali solutions. Silica is decomposed by hydrofluoric acid and by fusion with the fixed alkali carbonates or hydroxides.

**General Considerations.** — The natural and artificially prepared silicates may be grouped under two classes: 1. Those which are decomposed by acids. 2. Silicates not decomposed by acids. The Minerals datolite, natrolite, olivine and many basic slags are representative of the first class, and feldspar, orthoclase, pumice and serpentine are representative of silicates not decomposed by acids. The first division simply require an acid treatment to isolate the silica, the latter class require fusion with a suitable flux.

In technical analysis, in cases where great accuracy is not required, the residue remaining, after certain conventional treatments with acids, is classed as silica. This may consist of fairly pure silica or a mixture of silica, undecomposed silicates, barium sulphate and certain acid insoluble compounds. For accurate analyses this insoluble residue is not accepted as pure silica, unless impurities, which are apt to be found with the silica residue, are known to be absent from the material under examination.

Although the procedure for isolation of silicon is comparatively simple, errors may arise from the following causes:

1. Imperfect decomposition of the silicate.
2. Loss of the silicon by spurting when acid is added to the carbonate fusion.
3. Slight solubility of silica, even after dehydration, especially in presence of sodium chloride and magnesia.
4. Loss due to imperfect transfer of the residue to the filter paper.
5. Mechanical loss during ignition of the filter and during the blasting, due to the draft whirling out the fine, light silica powder from the crucible.
6. Error due to additional silica from contaminated reagents or from the porcelain dishes or glassware in which the solution was evaporated. A blank of 0.01% on the sodium carbonate will make an error of 0.1% per gram sample in an ordinary fusion where 10 grams of the flux are required.

7. Error due to loss of weight of the platinum crucible during the blasting.

8. Incomplete removal of water, which is held tenaciously by the silica. Furthermore, weighing of the residue should be done quickly, as the finely divided silica tends to absorb moisture.

Two general procedures will be given for treatment of the acid decomposable and undecomposable silicates. It is frequently advisable to use these two procedures in conjunction, extracting the material first with acid, and then fusing the insoluble residue with sodium carbonate; this procedure is used when a gritty residue remains after the acid extraction.

## DECOMPOSITION OF THE MATERIAL, GENERAL PROCEDURES

### Silicates Decomposed by Acids

**Acid Extraction of the Silicates.** — 0.5 to 1 gram of the finely pulverized material placed in a beaker or casserole is treated with 10 to 15 cc. of water and stirred thoroughly to wet the powder.[1] It is now treated with 50 to 100 cc. of strong hydrochloric acid and digested on the water bath for fifteen or twenty minutes with the beaker or casserole covered by a watch-glass. If there is evidence of sulphides (pyrites), etc., 10 to 15 cc. of concentrated nitric acid are now added and the containing vessel again covered. After the reaction has subsided, the glass cover is raised by means of riders and the mixture evaporated to dryness on the water bath. (This evaporation may be hastened by using a sand bath, boiling down to small bulk at comparatively high temperature, then to dryness on the water bath. Decomposition is complete if no gritty particles remain. A flocculent residue will often separate out during the digestion, due to partially dehydrated silicic acid, hydrated silicic acid, $Si(OH)_4$, is held in solution.) The silicic acid is converted to silica, $SiO_2$, the residue taken up with dilute hydrochloric acid, silica filtered off, washed with water, acidified with hydrochloric acid, and estimated according to the procedure given later.

### Silicates Not Decomposed by Acids

**Fusion with Sodium Carbonate or Sodium Bicarbonate.** — 0.5 to 1 gram of the air-dried, pulverized sample is placed in a large platinum crucible or dish in which has been placed about 5 grams of an-

[1] Water is added to the sample and then acid, as strong acid added directly would cause partial separation of gelatinous silicic acid, which would form a covering on the undecomposed particles, protecting them from the action of the acid.

hydrous sodium carbonate. The sample is thoroughly mixed with the carbonate by stirring with a dry glass rod, from which the adhering particles are brushed into the crucible. A little carbonate is sprinkled on the top of the mixture and the receptacle covered. It is heated to dull redness for five minutes and then gradually heated up to the full capacity of a Meker burner. When the mix has melted to a quite clear liquid, which generally is accomplished with twenty minutes of strong heating, a platinum wire with a coil on the immersed end is inserted in the molten mass, and this allowed to cool. The fusion is removed by gently heating the crucible until the outside of the mass has melted when the charge is lifted out on the wire, and after cooling disintegrated by placing it in a beaker containing about 75 cc. dilute HCl (1 part HCl to 2 parts of $H_2O$), covering the beaker to prevent loss by spattering. The crucible and lid are cleaned with dilute hydrochloric acid, adding this acid to the main solution. When the disintegration is complete, the solution is evaporated to dryness and silica is estimated according to directions given later.

If decomposition is incomplete, gritty material will be found in the beaker upon treatment of the fusion with dilute acid. If this is the case, it should be filtered off and fused with a second portion of sodium carbonate, and the fusion treated as directed above.

Notes. Fusions with soluble carbonates are generally best effected with the sodium salt, except in fusions of niobates, tantalates, tungstates, where the potassium salt is preferred on account of the greater solubility of the potassium compounds. Sodium alone has an advantage over the mixed carbonates, $Na_2CO_3 + K_2CO_3$, as silica has a high melting-point and a flux, which fuses at 810° C., is more apt to cause disintegration of the silicate than the mixture, which melts at 690° C.

Prolonged blasting is undesirable, as it renders the fusion less soluble. Aluminum and iron are also rendered difficultly soluble, when their oxides are heated to a high temperature for some time.

If the melt is green, it is best to dissolve out the adhering melt from the crucible with dilute nitric acid, as a manganate (indicated by the color), if present, will evolve free chlorine by its action on HCl and this would attack the platinum.

## PROCEDURE FOR THE DETERMINATION OF SILICON AND SILICA

As has been stated, the gravimetric method for determination of silica is the only satisfactory procedure for estimation of this substance. The oxidation of the element and its isolation have been dealt with in the section Preparation and Solution of the Sample. The following directions are for purification and final weighing of the element in the form of its oxide, silica, $SiO_2$.

**Extraction of the Residue — First Evaporation.** — The residue, obtained by evaporation of the material after decomposition of the silicate, by acids or by fusion, as the case required, is treated with 15–25 cc. of hydrochloric acid (sp. gr. 1.1), covered, and heated on the water bath 10 minutes. After diluting with an equal volume of water, filtration is proceeded with immediately, and the silica is washed with a hot solution consisting of 5 cc. of hydrochloric acid (sp. gr. 1.2) to 95 cc. of water and finally with water. This filtration may be performed with suction. The filtrate and washings are evaporated to small volume on a sand bath and then to dryness. This contains the silica that dissolved in the first extraction.

**Second Evaporation.** — The residue obtained from evaporation of the filtrate is dehydrated for 2 hours at 105–110° C. and extracted with 10 cc. of hydrochloric acid (sp. gr. 1.1), covered, and heated on the water bath for ten minutes diluted to 50 cc. with cold water and filtered immediately, without suction. The residue is washed with cold water containing 1 cc. of concentrated hydrochloric acid to 99 cc. of water, the washed residue containing practically all the silica, that went into solution in the first extraction, is combined with the main silica residue. This is gently heated in a platinum crucible until the filters are thoroughly charred, and then ignited more strongly to destroy the filter carbon and finally blasted over a Meker burner for at least thirty minutes, or to constant weight, the crucible being covered. After cooling, the silica is weighed. For many practical purposes this residue is accepted as silica, unless it is highly colored. For more accurate work, especially where contamination is suspected (silica should be white), this residue is treated further.

**Estimation of True Silica.** — Silica may be contaminated with $BaSO_4$, $TiO_2$, $Al_2O_3$, $Fe_2O_3$, $P_2O_5$ combined (traces of certain rare elements may be present). The weighed residue is treated with 3 cc. of water, followed by several drops of concentrated sulphuric acid and 5 cc. of hydrofluoric acid, HF (hood). After evaporation to dryness, the crucible is heated to redness and again cooled and weighed. The loss of weight represents silica, $SiO_2$.

Notes. Lenher and Truog make the following observations for determining silica: [1]

[1] Victor Lenher and Emil Truog, Jour. Am. Chem. Soc., 38, 1050, May, 1916.

1. In the sodium carbonate fusion method with silicates, there is always a non-volatile residue when the silica is volatilized with HF and $H_2SO_4$.
2. The non-volatile residue contains the various bases, and should be fused with sodium carbonate and added to the filtrate from the silica when the bases are to be determined.
3. In the dehydration of the silica from the hydrochloric acid treatment of the fusion, the temperature should never be allowed to go above 110°.
4. Dehydrated silica is appreciably soluble in hydrochloric acid of all strengths. With the dilute acid used, this error is almost negligible.
5. Dehydrated silica is slightly soluble in solutions of the alkaline chlorides. As sodium chloride is always present from the sodium carbonate fusion, an inherent error is obviously thus introduced.
6. The dehydrated silica along with the mass of anhydrous chlorides must not be treated first with water, since hydrolysis causes the formation of insoluble basic chlorides of iron and aluminum, which do not dissolve completely in HCl.
7. Hydrochloric acid (sp.gr. 1.1) in minimum amount should be used first to wet the dehydrated chlorides and should be followed by water to bring the volume to about 50 cc., after which the silica should be filtered off quickly.
8. Pure silica comes quickly to constant weight on ignition. Slightly impure silica frequently requires long heating with the blast flame in order to attain constant weight, and is then commonly hydroscopic.
9. Evaporations of the acidulated fusion in porcelain give practically as good results as when platinum is used.
10. Filtration of the main bulk of the silica after one evaporation is desirable, inasmuch as the silica is removed at once from the so lutions which act as solvents.
11. Dehydration of the silica under reduced pressure has no advantages over the common evaporation at ordinary atmospheric pressure.
12. Excessive time of dehydration, viz., four hours, possesses no advantages.
13. Excessive amounts of sodium carbonate should be avoided, since the sodium chloride subsequently formed exerts a solvent action on the silica. The best proportions are 4–5 of sodium carbonate to 1 of silicate. Less than 4 parts of sodium carbonate is frequently insufficient to decompose many silicates.
14. The non-volatile residue has been found to be invariably free from sodium. Pure silica, on fusion with sodium carbonate, subsequently gives no non-volatile residue.

**Fluorides.** — In presence of fluorides the melt is extracted with water (an acid extraction would volatilize some of the silica), and the extract filtered off from the insoluble carbonates. To the filtrate is added about 5 grams of solid ammonium carbonate, and the mix warmed to 40° C and allowed to stand for several hours. The greater part of the silica is precipitated. This is filtered off and washed with water containing ammonium carbonate. Preserve this with the insoluble carbonate for later treatment. The filtrate, containing small amounts of silicic acid, is treated with 1 to 2 cc. of ammoniacal zinc oxide solution (made by dissolving C.P. moist zinc oxide in ammonia water). The mixture is boiled to expel ammonia and the precipitate of zinc silicate filtered off. The precipitate is washed into a beaker through a hole made in the filter, and the adhering material dissolved off with dilute HCl, enough being added to dissolve the remaining residue. This is evaporated to dryness and silica separated as usual. Meantime the insoluble carbonate is dissolved with HCl, evaporated to dryness and any silica it contains recovered. Finally all three portions of silica are combined, ignited and silica estimated as usual.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Analysis of Silicate of Soda

**Determination of $Na_2O$.** — Five grams of the sample are dissolved in about 150 cc. of water and heated; 1 cc. of phenolphthalein is added and then an excess of standard sulphuric acid from a burette. The excess acid is titrated with standard sodium hydroxide to a permanent pink.

$$H_2SO_4 \times 0.6321 = Na_2O.$$

**Silica.** — Ten grams of the sample are acidified with hydrochloric acid and evaporated to dryness on the steam bath. The treatment is repeated with additional hydrochloric acid and then the residue taken up with 5 cc. of the acid and 200 cc. of water. The residue is digested to dissolve the soluble salts, filtered, washed and ignited. Silica is determined by loss of weight by volatilization of the silica with hydrofluoric and sulphuric acids. The filtrate is made to 1 liter.

**Iron and Aluminum.** — Five hundred cc. (5 grams) of the filtrate from the silica determination are oxidized with $HNO_3$ and the iron and aluminum precipitated with ammonia, washed, ignited and weighed as $Fe_2O_3$ and $Al_2O_3$. The residue is dissolved by digestion with hydrochloric acid or by fusion with sodium acid sulphate, and subsequent solution in hydrochloric acid. Iron is determined by titration in a hot hydrochloric acid solution with standard stannous chloride, $SnCl_2$, solution as usual. If only a small amount of precipitate of iron and alumina is present, as is generally the case, solution by hydrochloric acid is preferable to the fusion with the acid sulphate. The latter is used with larger amounts of the oxides.

**Lime, CaO.** — This is determined in the filtrate from iron and alumina by precipitation as the oxalate and ignition to CaO.

**Magnesia, MgO.** — This is determined in the filtrate from lime by precipitation with sodium ammonium phosphate. The precipitate is ignited and weighed as $Mg_2P_2O_7$ and calculated to MgO. Precipitate $\times$ 0.3621 = MgO.

**Combined Sulphuric Acid** — One hundred cc. of the filtrate from the silica determination (= 1 gram) is treated with $BaCl_2$ solution and sulphuric acid precipitated as $BaSO_4$.

$$BaSO_4 \times 0.4202 = H_2SO_4 \quad \text{or} \quad \times 0.3430 = SO_3.$$

**Sodium Chloride.** — Ten grams of the silicate of soda are dissolved in 100 cc. of water and made acid with $HNO_3$ in slight excess and then alkaline with MgO. Cl is titrated with standard $AgNO_3$ solution.

**Water.** — This is determined either by difference or by taking 10 grams to dryness and then heating over a flame and blasting to constant weight.

NOTE. For detailed procedures for each of the above see special subject.

### Analysis of Sand, Commercial Valuation

**Silica.** — Two grams of the finely ground material are fused in a platinum crucible with 10 grams of fusion mixture ($K_2CO_3 + Na_2CO_3$) by heating first over a low flame and gradually increasing the heat to the full blast of a Meker blast lamp. When the fusion has become clear it is cooled by pouring on a large platinum cover. The fused mass on the cover and that remaining in the platinum crucible are digested in a covered beaker with hot hydrochloric acid on the steam bath. The solution is now evaporated to dryness, taken up with a little water and 25 cc. of concentrated HCl and again taken to dryness. Silica is now determined by the procedure outlined under the general method.

**Ferric Oxide and Alumina.** — The filtrate is oxidized with crystals of solid potassium chlorate, $KClO_3$, and iron and aluminum hydroxides precipitated with ammonia. The precipitate is filtered, washed, ignited and weighed as $Fe_2O_3 + Al_2O_3$.

**Calcium Oxide.** — To the ammoniacal filtrate 10 cc. of ammonium oxalate solution are added, the solution heated to boiling and the precipitate allowed to settle until cold. The solution should not be over 200 cc. The calcium oxalate is filtered off, washed and ignited. The residue is weighed as CaO.

**Magnesium Oxide.** — The filtrate from the lime is made strongly ammoniacal and 10 cc. of sodium ammonium phosphate added. The solution during the addition is allowed to stand cold for some time, at least an hour. The precipitate is filtered and washed with dilute ammonia (1 of reagent to 3 parts of water), then ignited and weighed as $Mg_2P_2O_7$. This weight multiplied by 0.3621 = MgO.

For more detailed directions see the individual subjects under the chapters devoted to the element.

## SILVER

**Ag, at.wt. 107.88; sp.gr. 10.50–10.57; m.p. 960.5° C.; b.p. about 1950° C.; oxides, $Ag_2O$, $Ag_4O$, $Ag_2O_2$**

Silver is determined in copper, lead, silver, sulphur or other ores, in copper and lead furnace by-products, and in lead by furnace assay methods, in which a preliminary acid treatment of the sample is rarely employed; in native copper ore, in copper, copper alloys, gold, gold alloys and in the slime from the electrolytic refining of copper or lead by furnace methods, in which a preliminary acid treatment of the sample is employed, in silver alloys by volumetric or gravimetric methods; in mercury by a gravimetric method; in cyanide mill solution or solutions containing much organic matter by furnace process on the residue obtained by evaporation or precipitation; in silver plating electrolyte by electrolysis.

### OCCURRENCE

Silver is found as metallic silver, often in large pieces, but more commonly in combination as silver glance, argentite, silver-copper glance, stromeyerite, etc. Among the more important minerals are the following:

**Minerals.** — *Native Silver.* — The metal may be alloyed with Au, Pt, Cu, Sb, Hg, Bi. Silver is a white, malleable metal, tarnishing brown to nearly black, it is opaque and has a metallic lustre; streak silver white; hardness 2.5–3. The metal occurs in scales, twisted filaments, and in masses. The metal on charcoal fuses in the blowpipe flame to a white metallic globule. Silver dissolves in nitric and in sulphuric acid. Hydrochloric acid added to the silver solution precipitates a white curdy compound AgCl, which darkens on exposure to the light.

*Argentite*, Silver Glance, $Ag_2S$, is a soft, black, opaque, sectile mineral, with metallic lustre; lead-gray streak; hardness 2–2.5. It occurs as masses, grains or as incrustations.

*Hessite*, $(Ag.\ Au)_2Te$, a fine grained, massive, opaque mineral with metallic lustre, steel-gray; streak, black; hardness 2–2.5. The crystals are also coarse granular.

*Proustite*, Light Ruby Silver, $3Ag_2S.As_2S_3$, a brittle, translucent to transparent, scarlet-vermillion color with similar colored streak; adamantine to brilliant lustre; hardness 2–2.5.

*Pyrargyrite*, Dark Ruby Silver, $3AgS.Sb_2S_3$, a black opaque, or translucent mineral purple-red by transmitted light; brittle; purple-

red streak; hardness 2.5. Usually occurs massive or in films, may be crystalline.

*Cerargyrite*, Horn Silver, AgCl, a pearl gray, greenish mineral which darkens in the light to violet, brown and finally black; translucent; sectile; lustre, resinous; shining white streak; hardness 1–1.5.

Other minerals *Amalgam*, $Ag_2Hg_3$ to $Ag_{36}Hg$; *Stromeyerite*, $(CuAg)_2S$; *Stephanite*, $Ag_5SbS_4$; *Polybasite*, $9Ag_2S.Sb_2S_3$; *Bromyrite*, AgBr; *Embolite*, Ag(Br,Cl); *Iodyrite*, AgI.

## SUGGESTION TO STUDENTS

Determine silver in a solution of silver nitrate or in a silver alloy dissolved in nitric acid, both gravimetrically as silver chloride and volumetrically, preferably by Volhard's Thiocyanate method as outlined under the methods for silver.

## DETECTION

A trace of silver in most substances is detected with greatest certainty by furnace assay methods.

*The wet method* of detection of silver most commonly practiced, depends upon observation of the properties of the precipitate formed by the addition of a not excessive amount of alkaline chloride to a cold nitric or sulphuric acid solution of the substance undergoing examination. One-tenth milligram of silver precipitated as silver chloride in a cold 200 cc. acid solution gives a very perceptible opalescence to the liquid.

*Silver chloride* is white when freshly precipitated, tinted pink when palladium is present; in colorless liquids on exposure to light turns brown, violet, blue or black. By agitation, heating or long standing the precipitate becomes coagulated or granular and in such a state is retained by an ordinary filter. The presence of some forms of organic matter prevents coagulation.

Silver chloride is dissolved by concentrated hydrochloric acid; raising the temperature of the acid assists the action. It is dissolved by sodium thiosulphate, alkali cyanides, mercuric nitrate, and alkaline chlorides.

From mercurous chloride, silver chloride, except when constituting a small proportion of the precipitate, is distinguished by its solubility without decomposition in ammonia. Precipitation from its ammoniacal solution is accomplished by acidifying. Lead chloride, precipitable also by hydrochloric acid, is not flocculent, does not coagulate, but dissolves quite freely by heating. Addition of hydrochloric acid to a solution of silicon, tellurium, thallium, tungsten or molybdenum may produce a precipitate, in each case, easily distinguishable from that of silver chloride, but may mask traces of the salt.

Silver, in a cold solution containing free nitric acid, only a small amount of colored salts and no mercury, may be detected through

the formation of a white precipitate, similar in appearance to silver chloride, by addition of a slight excess of an alkaline thiocyanate.

When a solution of silver salt is added to a mixture of 20 cc. ammonium salicylate (20 grams. of salicylic acid neutralized with ammonia, a slight excess added and the whole made up to 1000 cc.) and 20 cc. of a 5% solution of ammonium persulphate added, an intense brown color is produced, which will detect the presence of a 0.01 milligram of silver. Lead does not affect the test.

When it appears that the chloride or thiocyanate test for silver is not positive on account of the presence of other precipitable elements, the precipitate, after it settles, is filtered through the finest quality of paper, and the mixture of the ash of the incinerated filter with dry potassium carbonate heated on charcoal with a mouth blowpipe. If silver is present and not associated with a large amount of palladium, there will be found on the charcoal pellicles of the color characteristic of silver, which have no white or yellow sublimate when melted in the oxidizing flame of the blowpipe. The pink palladium salts of silver precipitated by a chloride or thiocyanate before the blowpipe produces metal which is dull in appearance and not readily melted.

Notes. Silver may be recognized in a solution of concentration 1 to 240,000 by the reduction of its salts with alkaline formaldehyde. Whitby's method of detection and estimation of small amounts of silver depends upon the formation of a yellow color through addition of sucrose and sodium hydrate. Ammonium hydrate interferes, but bismuth, cadmium, copper, mercury of either valence, lead or zinc, in amounts equal to that of the silver, do not. Malatesta and DeNola add to the solution to be tested a few drops of a solution of nitrate of chromium and then potassium hydrate to alkalinity. A brownish turbidity or black precipitate of silver oxide forms. The limit of sensitiveness is 0.5 milligram in 100 cc.

## GRAVIMETRIC METHODS FOR THE DETERMINATION OF SILVER

### PRECIPITATION AS SILVER CHLORIDE

**Introductory.** — Although silver might be determined as an iodide or bromide, the fact that these halides are more sensitive to light than the chloride, and decompose more readily, with liberation of the halide and the formation of sub-halides, has led to the precipitation of silver as the chloride.

**Reaction.** $AgNO_3 + HCl = HNO_3 + AgCl$.

**Reagents.** *Hydrochloric Acid.* — One volume of strong HCl (sp.gr. 1.19) diluted with five volumes of water (sp.gr. of dilute HCl 1.035); 1 cc. contains 0.074 g. of HCl, equivalent to 0.219 g. of Ag.

*Nitric Acid.* — One volume of strong $HNO_3$ diluted with 1.6 volumes of water. (sp.gr. of acid is 1.2) 1 cc. contains 0.38 g. of $HNO_3$, which would dissolve 0.64 g. of Ag.

1. **Preparation of the Sample. — Solution.** *Silver Alloys.* — Place 0.5–1.0 gram of the alloy in an Erlenmeyer flask and add 5 cc. of the dilute nitric acid. Heat gently until the alloy is dissolved and the brown fumes are expelled. The solution is now diluted to about 100 cc. and the silver precipitated as stated below.

*Soluble Silver Salts.* — The salt is weighed into a weighing bottle; 1.0–2.0 grams are sufficient for a determination. The solution is now diluted to about 100 cc. and the silver precipitated as stated below.

*The Halides of Silver.* — These are best brought into solution by fusion with about six times the weight of the sample of sodium carbonate. This converts the silver into the carbonate and the halide combines with sodium and is dissolved out in water. The silver carbonate is washed free of the halide and then dissolved out in dilute nitric acid.

*Ores of Silver.* — These may be brought into solution by digestion with nitric acid, the residue remaining is treated as stated above under halides of silver. Unless the ore is very high in silver it is preferable to make the analysis by Fire Assay.

2. **Precipitation of Silver Chloride.** — Heat the solution to boiling and add from a burette drop by drop, 5 cc. of dilute hydrochloric acid. This is sufficient to precipitate over 1 gram of silver. The excess of acid is desired as the chloride is less soluble in free hydrochloric acid.

Note. The chloride is soluble in strong hydrochloric acid, hence a large excess is undesirable. Shaking or vigorously stirring the mixture will clear a cloudy solution. This is necessary to coagulate the silver chloride, as the fine suspended silver chloride will pass through the filter paper.

3. **Filtration: (Procedure if Filter Paper is Used).** — Decant the clear solution into the filter. Test the filtrate with a drop of dilute HCl to make sure all the silver is precipitated. Now wash two or three times by decantation, using hot water containing 1 cc. of $HNO_3$ per 100 cc. of distilled water. Transfer the silver salt to the filter and

continue washing until free from chlorides. Six to eight additional washings should be sufficient.

4. *Dry* the filter and silver salt in the oven at 100–110 degrees C.

5. *Remove* as much of the silver chloride as possible from the paper, placing the salt on a glazed sheet of paper, covering it with a watch glass.

6. *Ignite* the filter in a crucible (whose weight has been ascertained), then add to the ash a drop of nitric acid and a drop of hydrochloric acid. Heat gently to expel the acids. (Handle the crucible with tongs. Do not place on the table.)

7. *Transfer* the chloride from the glazed paper to the crucible and heat gently until the salt just begins to fuse on the sides of the crucible.

8. *Cool* in a desiccator for fifteen to twenty minutes.

9. *Weigh* as AgCl, making an allowance for the weight of the crucible. AgCl $\times$ 0.7526 gives the weight of Ag in the salt.

10. Calculate the per cent silver from the weight of sample taken.

3a. **Procedure if a Gooch Crucible is Used.** — Prepare a Gooch crucible with a fairly thick pad of asbestos fibre (1/8 in. thick). Wash once with alcohol and dry to constant weight at 110 degrees C. Keep a record of the weight.

4a. *Wash* the precipitate by decantation, pouring the washings through the Gooch, with application of suction. Transfer the chloride to the crucible and wash free of chlorides.

5a. *Finally* wash once with alcohol and dry at 110 degrees C. to constant weight.

6a. *Calculate* the percentage of silver as directed in the first method.

Notes. *Solubility* of the silver halides. Milligrams of salt per 100 cc. of water. AgCl 0.00017; AgBr 0.00004; AgI 0.00001.

*Interferences.* — Antimony, mercury, and lead interfere and should be removed if present.

*Paper* is separated in the first procedure as the carbon reduces the salt to metallic silver, causing low results.

*Gooch.* — If the asbestos fibre is poor a loss of the fibre will occur during washing of the precipitate, causing low results.

*Light.* — Strong light will affect the salt causing the formation of the subhalide of silver and the liberation of chlorine. A drop of nitric followed by a drop of hydrochloric acid will restore the original form. This treatment is necessary only when a dark colored salt is obtained by light action.

*Large Samples.* — It is frequently advisable to dissolve larger samples than stated. The solution is made to 500 cc. and a portion taken for analysis.

**Solubility.** — Nitric acid, dilute or concentrated, attacks silver rapidly when hot. The presence of a soluble chloride, iodide or bromide in the solvent or substance will retard and may prevent solution. Unless oxidizing agents are present, dilute sulphuric acid has practically no action on massive silver, but hot, strong acid commences to be an active solvent at a concentration of 75% $H_2SO_4$. Hydrochloric acid attacks silver superficially. The action of alkaline hydrates or carbonates in solution is inappreciable; in a state of fusion, slight.

### DETERMINATION AS SILVER CYANIDE

In the analysis of mercury, the nitric acid solution of the metal is nearly neutralized with a solution of sodium carbonate. Potassium cyanide solution is then added until the precipitate, which first forms, is dissolved. Then under a hood with strong draft, dilute nitric acid is added in slight excess of the quantity required to combine with the base in the amount of potassium cyanide present. The precipitate of silver cyanide, practically insoluble in dilute nitric or hydrocyanic acid, is coagulated by stirring or long standing and filtered from the cold solution of mercuric nitrate by use of a tared paper-bottomed Gooch crucible. The precipitate is washed with cold dilute nitric acid (1–10) until a test of the washings with hydrogen sulphide shows the absence of mercury. The crucible is dried at 100° to constant weight.

$$AgCN \times 0.8057 = Ag.$$

NOTES. Determination of silver as metal through precipitation with hypophosphorous acid [1] as silver sulphide or as silver chromate [2] are methods of doubtful technical application.

### Electrolytic Method

According to the strength of the silver bath 10 or 20 cc. are filtered into a tared 200 cc. platinum dish and according to the greater or smaller excess of cyanide present, 0.1 to 1 gram of potassium cyanide in solution is added. The electrolyte diluted to about a half inch from the edge of the dish is kept, by a flame underneath, at a temperature of 60° — 65° C. during the period of electrolysis at $N.D._{100}$ = 0.08 amp.

Complete precipitation, which requires three to three and a half hours, is recognized by test with ammonium sulphide. Without interruption of the current, by use of a siphon, displacement of the electrolyte with water is accomplished. The dish is rinsed with alcohol and ether, dried at 100° C., weighed and silver obtained calculated to grams per liter or cubic foot.

NOTES. Benner and Ross [4] deposit 0.15 gram in twenty minutes with a current of 3 amperes from 50 cc. of electrolyte containing 8 grams of potassium cyanide and 2 grams of potassium hydrate on a 9-gram platinum gauze cathode.

Exner using a platinum dish as the cathode and a 2 in. diameter bowl-shaped spiral anode revolving 700 R.P.M., deposited 0.4900 gram from about 125 cc. of a hot electrolyte containing 2 grams potassium cyanide in ten minutes at $N.D._{100}$ 2 amps.

The above methods presume the absence of other metals precipitable under the conditions mentioned.

---

[1] Mawrow and Mollow, Zeit anorg. Chem., 61, 96.
[2] Gooch and Bosworth, Am. J. Sci., 27, 241.
[3] Langbein, "Electro-Deposition of Metals," 6th Ed.
[4] J. A. C. S., July, 1911, 1106.

## VOLUMETRIC METHODS FOR DETERMINATION OF SILVER

### VOLHARD'S THIOCYANATE METHOD

This method is especially adapted to the determination of silver in cold dilute nitric acid solution. The method is based on the greater affinity of silver ions than ferric for thiocyanate ions. When the silver has been precipitated as thiocyanate the ferric indicator reacts with the thiocyanate producing the characteristic red color.

**Reactions:** $AgNO_3 + KCNS = KNO_3 + AgCNS$ ppt.

$$Fe(NO_3)_3 + 3KCNS = 3KNO_3 + Fe(CNS)_3 \text{ red}$$

NOTE. Mercury and palladium, highly colored salts of cobalt and nickel, copper if over 60% in the sample, nitrous acid and chlorine interfere and should be absent.

**Standard Solution.** — *Ferric Indicator.* — Make 100 cc. of a saturated solution of ferric ammonium sulphate or ferric sulphate. Add sufficient $HNO_3$ (freed from nitrous acid by heating) to clear up the solution and produce a pale yellow color, 5 cc. of this reagent is used in a test.

**Standard Silver Solution.** — A N/10 solution contains per liter 10.788 grams of silver, or 16.989 grams of $AgNO_3$. A solution containing 0.005 grams of Ag per cc. is a convenient strength.

Dissolve 1.0 gram of pure silver foil in 10 cc. of dilute $HNO_3$, 1:1.6 (sp.gr. 1.2). Boil to expel the nitrous oxides and dilute to 200 cc. 1 cc. will contain 0.005 grams of silver.

**Thiocyanate Reagent.** — Dissolve 7.4 grams $NH_4CNS$ or 9.2 grams of KCNS in water and dilute to 1,000 cc. Standardize the solution against the standard silver solution.

**Standardization.** — Measure 50 cc. of the standard silver solution into a beaker or an Erlenmeyer flask and dilute to 100 cc.

Add 5 cc. of the ferric indicator.

Titrate with the thiocyanate reagent until a permanent red tint is obtained. Each addition of the reagent will produce a temporary red color which fades immediately as long as any silver remains uncombined with the thiocyanate. A trace of excess of the reagent produces a permanent faint red color.

Note the cc. required and calculate the value of 1 cc. in terms of silver. 50 cc. of the standard silver solution contains 0.25 g. of Ag.

Some prefer to have the thiocyanate exactly equal in strength to the silver solution. Should this be desired, dilute to the necessary volume and again standardize against the silver solution.

The value of 1 cc. should be recorded on the container.

### Determination of Silver in the Unknown

Weigh 0.25–0.3 gram of the alloy and dissolve in an Erlenmeyer flask by addition of 5 cc. of dilute $HNO_3$ (sp.gr. 1.2) Heat to expel lower oxides.

Cool, dilute to about 100 cc. and add 5 cc. of the ferric indicator.

Titrate with the standard thiocyanate reagent to a permanent faint red color.

From the cc. of the reagent used, calculate the amount of silver present in the sample taken.

Divide the result by the amount of sample taken and multiply by 100 = per cent Ag. in the alloy.

## GAY-LUSSAC METHOD

This very accurate method is especially adapted to the valuation of silver bullion, but may be applied in principle to the determination of silver in a nitric acid solution which contains as little as 100 milligrams of the metal, providing the volume of the solution is not so large or color so deep as to make a precipitate of silver chloride equivalent to 0.1 milligram of silver indistinguishable. Metals that interfere are mercury and tin.

The method is founded upon the almost absolute insolubility of silver chloride or bromide in cold dilute nitric acid and the property of the precipitate becoming so completely coagulated through agitation that it settles speedily, leaving a liquid sufficiently clear to permit of observance of any precipitate produced by further addition of precipitant.

**Reactions:** $AgNO_3 + NaCl = NaNO_3 + AgCl \downarrow$

$AgNO_3 + NaBr = NaNO_3 + AgBr \downarrow$

The use of a bromide is preferable to a chloride salt as a reagent, chiefly because on account of the greater insolubility of silver bromide, the end-point of the operation of titration is more sharply defined.

The presence of free sulphuric acid is prejudicial to a very close determination, because of the volume of liquid required to keep silver sulphate in solution, and also because the result of agitation after addition of precipitant, is apt to be a fine precipitate which does not readily settle.

**Reagents.** — *The decimal salt solution* is best made from C.P. salts, either 0.5149 gram of sodium chloride or 1.1033 grams of potassium bromide per liter.

*The decimal silver solution* is made by dissolving 1 gram of pure silver with a few cc. of nitric acid and making up to 1 liter with distilled water.

The factor of volume change per degree change of temperature from 15 to 21° C. is approximately 0.00012; from 20 to 26°, 0.00019; from 25 to 31° C., 0.00024.

Although the approximate precipitating value should be known by previous test, it is the better practice to determine the exact value by running two or more checks of pure silver simultaneously with each batch of assays than to apply the temperature correction factor.

**Apparatus.** — The apparatus required consists of a pipette which will deliver approximately 100 cc. with an accuracy of not over 5

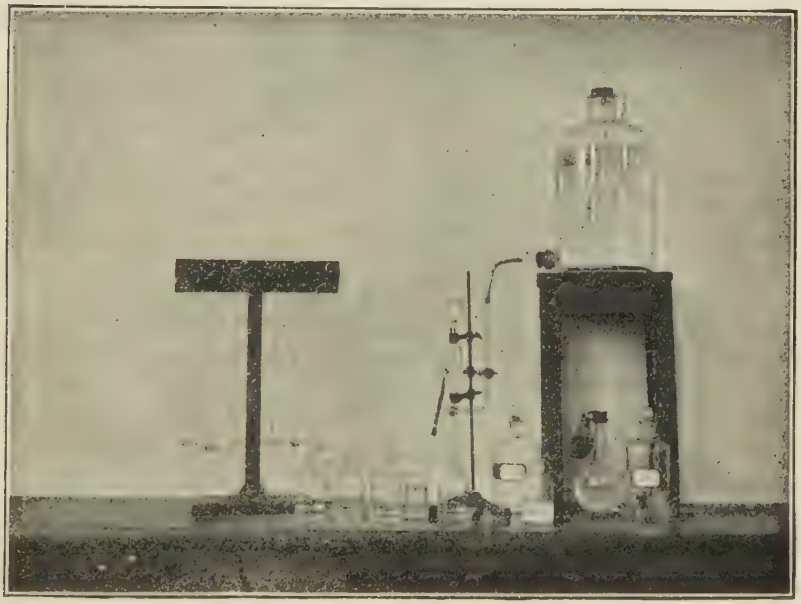


Fig. 104. Apparatus for Determining Silver. Gay-Lussac Method.

milligrams variation in weight of the standard solution at constant temperature between successive deliveries, 10 cc. burettes with glass stopcocks; and 8-oz. narrow mouth, round, flint-glass bottles with high, tightly fitting stoppers; the assay bottles should be of a quality which will endure heating in a steam bath or on a hot plate.

Since the end-point by the Gay-Lussac method depends upon the observance of cessation of precipitation, it is evident, in order to avoid undue tediousness in its operation, that the silver content of the amount of sample taken for assay should be known within a few milligrams.

**Procedure.** — The approximate silver value having been determined, such an amount of the sample is weighed out and placed in an assay bottle, as will contain silver in slight excess of the silver equivalent of the pipette full of standard salt solution. Ten to 15 cc. of nitric (1.26 sp.gr.) acid are added and the bottle kept in a steam bath or on a moderately hot plate until solution of silver is complete.

To the cold solution of the sample is added a pipette full of the standard salt solution and the tightly stoppered bottle agitated until the precipitate will settle with sufficient completeness to permit of observance of any turbidity produced by addition of either of the decimal solutions.

More agitation than is absolutely necessary should be avoided, because of the increasing tendency of the precipitate toward the fine granular form, which settles slowly.

On account of alteration of the character of the precipitate by sunlight, the titration should be carried out in a shaded place and as expeditiously as possible.

One-tenth cc. of the decimal salt solution is dropped into the bottle, and holding the bottle against a dark background, the appearance of the cloud of precipitate is noted.

From the character of the precipitate, after some practice, it is possible to judge whether a single cc. or more may be added at once, or whether the titration must be continued by one-tenth cc. additions.

Until the non-appearance of cloudiness indicates the end-point, the bottle should be agitated after each addition of salt solution.

If the pipette full of standard solution is more than sufficient to precipitate the silver, or in case the end-point has been run over, decimal silver solution is added in 1 cc. portions until precipitation ceases. Decimal salt solution is then added cautiously until the end-point is reached. Completion of the titration should always be with the decimal salt solution. Some confusion in judgment of the end-point may arise, on account of the fact that an excess of sodium chloride produces turbidity. The appearance of the cloud so produced is characteristic, and can be distinguished after some practice from that exhibited when silver is still in excess. If bromide standard and decimal solutions are used, excess of the reagent produces a turbid film only after long standing.

The silver value in milligrams of the standard solution, plus the number of cc. of decimal salt solution which produced a precipitate, minus the number of cc. of decimal silver solution added, gives the amount of silver in the quantity of sample weighed out.

The result calculated to milligrams silver per gram of sample is customarily reported in the case of silver bullion as points fineness.

The accuracy of the method is limited by the quality of pipette and the skill of the operator. With a pipette which delivers accurately an experienced operator can speedily make analyses in which the error is only of the order of plus or minus 0.1 milligram of silver.

## METHOD OF THE DENVER MINT

### U. S. Mint Modification of the Gay Lussac Method for Silver *

This method is used in all three of the United States Mints and the U. S. Assay Office, New York City, for determining silver in ingots and fine silver and has been found very satisfactory both as regards speed and accuracy.

**Standard Solutions.** — Two standard salt solutions are regularly used in the determinations. The first is called a " normal " and the second a " decimal " solution.

The first or " normal " solution is made of such concentration that 100 cc's of it will precipitate exactly 1002 milligrams of silver. 5.43 grams of C. P. sodium chloride are dissolved in water and diluted to make one liter of solution. It is kept in a large 40 liter carboy and is siphoned off as needed.[1]

The decimal solution is made by diluting 100 cc's of the " normal " solution to a liter.

#### Standardization

The normal solution must be standardized at frequent intervals because of temperature changes which affect the concentration of the solution. The factor of volume change per degree change of temperature from 15 to 21 degrees C. is approximately 0.00012; from 20 to 26 degrees, 0.00019; from 25 to 31 degrees, 0.00024.

The standardization is carried out as follows:

**Solution and Precipitation.** — A " proof " of 1004 milligrams of fine silver is carefully weighed out, placed in a glass stoppered 8 oz. bottle and dissolved in 10 cc's of 1:1 nitric acid on a hot plate. Then 100 cc's of " normal " salt solution, sufficient to precipitate 1002 grams of silver, are added from an upright stationary pipette. The pipette is filled by means of a siphon controlled by a stopcock convenient to the right hand. After filling, the left forefinger is placed over the pipette, the rubber hose connection removed from the bottom, and the bottle containing the dissolved proof placed underneath, when the forefinger

[1] 40 liters are made up at one time by the Denver Mint. The strength of the solution may be regulated by the size of the pipette used. At the Denver Mint 4.82608 grams per liter are taken of the C. P. NaCl, since the pipette delivers more than 100 cc.

* Communicated to the author by F. C. Bond, Humid Assayer, Denver Mint, Colorado.

is removed, allowing the contents to drain into the bottle, shaking the bottle once or twice to mix the solution. Then 2 cc's of the decimal solution are added by means of a small pipette graduated in cc's and held in the hand, and the stoppered bottle is placed in the shaker.

The shaker violently agitates the solution and causes the precipitate to coagulate and settle. The bottle is removed after four minutes.

More agitation than is absolutely necessary should be avoided, due to the increasing tendency of the precipitate to become granular and settle slowly.

**Titration.** — The bottle containing the coagulated precipitate is best placed upon a shelf in a window through which only reflected light enters, at such a height that the top of the solution is upon a level with or slightly above the eye. The shelf is backed by a blackened board which covers the window under the shelf and extends nearly to the top of the bottle.

The bottle stands a moment to allow the precipitate to settle and 1 cc. of the decimal salt solution is added from the hand pipette. The solution is shaken by moving the top of the bottle through a small arc once or twice and the reading is taken after 10 seconds. A slight white cloud forming at the top of the solution and more pronounced when viewed from below constitutes a " show " and indicates that only a small portion of the cc. added was needed to precipitate the remaining silver. This is the desired condition for a proof.

The reading is taken as a " show ", " quarter ", " half ", " three quarters ", and " one "; according to the portion of the cc. of salt solution necessary to precipitate the remaining silver. If the cloud is deep enough to indicate that all of the cc. has been used, the bottle should be placed in the shaker and the precipitate coagulated, after which another cc. is added and the reading taken as before with the addition of one cc.

The assignment of the proper value to the precipitate is difficult for the novice and experience in comparison is of much more value than any description could be. However it may be stated that a slight precipitate extending through the upper half of the solution after a slight uniform shake should be called a " quarter ", a precipitate of the same appearance throughout the solution is a " half ", a heavier precipitate throughout is called " three quarters ", while a still denser precipitate is read " one " and should be confirmed by shaking and adding another cc., which should yield a " show ", a very faint cloudiness.

The " show " of the proof influences the reading of the determinations and its appearance should be kept constantly in mind, since a " quarter " on a determination means that one quarter of a cc. more of the decimal salt solution was used in precipitating silver than was used in the proof. Thus the proof reading or " show " is taken as zero and the concentration of the " normal " solution should be adjusted so that the proof gives as light a show as possible.

**Procedure.** — In the following determinations it is advisable to run a standard of proof silver side by side with the sample bullion for comparative purposes.

**Fine Silver.** — For silver bullion 998 parts fine or above a sample of 1005 milligrams is weighed out, dissolved, precipitated and titrated as described under Standardization.

In case 1 cc. was added, gave a heavy precipitate, was agitated, and a second cc. added which gave a " half ", the reading would be $1\frac{1}{2}$ and the silver would be

$$\frac{1002 + 1\frac{1}{2}}{1005} = \frac{1003.5}{1005} = 998.5 \text{ fine.}$$

In case a large number of samples are to be run, tables may be prepared for each fourth of a cc. which will make the above calculation unnecessary.

**Coin Ingots.** — In determining the silver in silver coins or in silver coin ingots as they come from the melting room, which are usually within $1\frac{1}{2}$ points of 900 fine, the sample weighed is 1115 milligrams. The color given to the solution by the copper base need not interfere with the titration.

### Notes on the Method

Determinations may be made on silver bullion of almost any grade if the approximate fineness is previously determined by fire assay or the Volhard method. It is ordinary practice to weigh up the sample at the next higher even five milligrams above that calculated. Thus if it is found from preliminary assay that 1082 milligrams of bullion will contain approximately 1002 milligrams of silver, 1085 milligrams will be weighed out for a sample.

**Interfering Elements.** — There are very few substances which will be found in bullion in sufficient quantity to interfere with the process. The presence of free sulphuric acid is detrimental to a very close determination.

The use of a bromide is considered as preferable to a chloride as a reagent but the chloride is commonly used.

An eyeshade assists in making the readings accurately.

The chloride precipitate is reduced to a blue sub-chloride on standing in the sunlight so that the bottle should be exposed to the light as little as possible.

A set of twelve samples, with the bottles transported in a suitable wire frame, is usually run at one time.

A decimal solution of silver nitrate of equal strength with the decimal salt solution may be used for back titration, however the end-point is less distinct and it is advisable to weigh out a larger sample.

Duplicates are commonly run.

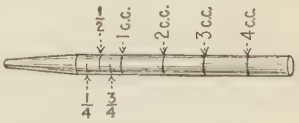



FIG. 105

Tables giving the fineness for different classes of materials examined for each reading facilitate calculations and are recommended for use.

To determine the $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$, a beginner should have a pipette, graduated

in 1 cc. holding 5 to 7 cc. length for hand use with one cc. divided in the $\frac{1}{4}$, $\frac{1}{2}$, $\frac{1}{3}$, and he should use the same until he is familiar with the density of precipitates produced by one cc. with silver equivalent to the above fractions.

Weight Taken 1115 mg.

| | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| 0 | 896.9 | 897.7 | 898.6 | 899.6 | 900.4 | 901.3 | 900.2 |
| $\frac{1}{4}$ | 897.1 | 898.0 | 898.9 | 899.8 | 900.7 | 901.6 | 902.5 |
| $\frac{1}{2}$ | 897.3 | 898.2 | 899.1 | 900.0 | 900.9 | 901.8 | 902.7 |
| $\frac{3}{4}$ | 897.5 | 898.4 | 899.3 | 900.2 | 901.1 | 902.0 | 902.9 |

No pipette is of use in the practice of the Gay-Lussac method which shows any tendency to spatter at the beginning or ending, or yields a quickly following or clinging drop at the completion of discharge. The film of liquid adherent to the inner surface of the body of a good pipette will drain without sign of rivulet effect and be retained by the capillary of the discharge tube for at least a minute.

## STRONTIUM

**Sr″, at.wt. 87.63; sp.gr. 2.54; m.p. 900° C; oxides SrO and $SrO_2$**

### OCCURRENCE

Strontium never occurs free in nature. It is found principally in the ores celestite, $SrSO_4$, and strontianite, $SrCO_3$. It generally accompanies calcium in the various forms of calcite and aragonite. It occurs with barium in barytocelestine, and is found in barytes. It also occurs associated with barium as a silicate in brewsterite, $Al_2O_3.H_4(BaSr)O_3.(SiO_2)_6.3H_2O$. It is found in traces in certain mineral waters and in sea-water.

**Minerals.** — *Strontianite*, $SrCO_3$, colorless, pale yellowish, or greenish white, also green and gray, brittle, translucent mineral with vitreous lustre; in masses of imperfect radiating needle-like crystals, also fibrous or granular; streak white; hardness, 3–3.5.

*Celestite*, $SrSO_4$, a white, translucent, nearly opaque mineral often with bluish or reddish tinge; brittle, pearly lustre; white streak; hardness 3–3.5. Occurs in tabular to prismatic crystals, cleavable masses and fibrous, rarely granular. Heavy resembling barite.

### DETECTION

Strontium is precipitated with barium and calcium, in the filtrate, from the ammonium sulphide group, by addition of ammonium carbonate to the ammoniacal solution. The precipitate is dissolved in acetic acid and treated with potassium dichromate, and the barium filtered off as $BaCrO_4$. Strontium and calcium in the filtrate are separated from the excess of potassium chromate by reprecipitation as carbonates by the addition of ammonium carbonate, the precipitate again dissolved in acetic acid and the excess of free acid neutralized with ammonia. Strontium may now be precipitated from the concentrated solution by boiling with an equal volume of a saturated solution of calcium sulphate.

**Sodium Sulphate Test.** — A saturated solution of the salt added to a solution containing strontium chloride, made strongly acid with acetic acid, and the mixture boiled, will produce a distinct precipitate if strontium exceeds 0.0015 normal. Calcium does not precipitate until 1.3 normality is reached.

**Flame Test.** — Strontium, preferably in the form of the chloride in a hydrochloric acid solution, placed on a platinum loop and held in a colorless flame, colors the flame crimson. (Lithium gives a red

color, calcium a yellowish-red.) The test is best confirmed by means of the spectroscope.

**The Spectra of Strontium.** — Eight bright bands; 6 are red, 1 orange, 1 blue. Two of these, known as strontium $\beta$ and $\gamma$, are red, the orange is strontium $\alpha$ and the blue strontium $\delta$. The delicacy of the test is 0.6 milligram of Sr per cc. The test is very much more delicate with the arc spectra, e.g., 0.03 milligram of Sr per cc. See chapter on barium, Preliminary Tests under Separations.

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

The following facts regarding solubility may be of value in the determination of strontium. 100 cc. of water dissolves 1.74 grams $Sr(OH)_2.H_2O$ at 20° C. The hydroxide is less soluble than that of barium. The peroxide dissolves to the extent of only 0.008 gram per 100 cc. 20° C. One hundred cc. of water dissolves 0.0011 gram [1] of $SrCO_3$(18°); 0.0114 gram of $SrSO_4$ at 18° and 0.0104 at 100°; the presence of sulphuric acid decreases this solubility, i.e., 0.00083 gram of $SrSO_4$; 0.0051 gram of $SrC_2O_4.H_2O$ at 18° and 5 grams at 100° C.; the presence of oxalic acid decreases this solubility. The sulphate dissolves in concentrated sulphuric acid, and is appreciably soluble in HCl, $HNO_3$, $HC_2H_3O_2$, $NH_4Cl$, $NH_4NO_3$, NaCl, $MgCl_2$. The carbonate and oxalate are soluble in mineral acids.

The procedure for the treatment of ores and strontium products is the same as those described for barium and calcium. We refer to the chapters on these elements for the preparation of the strontium solution.

**Separation of Strontium from Magnesium and the Alkalies.** — The procedure is the same as the one given in detail under barium for the separation of the alkaline earths from magnesium and the alkalies. Either the oxalic acid method or precipitation of strontium as a sulphate in presence of alcohol will accomplish this separation. If a sulphate precipitation is made it will be necessary to fuse the sulphate with sodium carbonate to get it into solution or to effect further separation from members of the ammonium carbonate group, should these be present.

**Separation of Strontium from Calcium.** [2] — Strontium and calcium are converted into the nitrates and taken to dryness and all water expelled by heating to 140° C. for an hour or more. The nitrates are now extracted with equal parts of absolute alcohol and anhydrous ether or by boiling with amyl alcohol at 130° C. (hood). Strontium remains insoluble and calcium goes into solution as the nitrate. Strontium nitrate may require further solution in water, evaporation to dryness, heating and extraction to remove calcium completely should this be present in large excess. The nitrate of strontium is

[1] Treadwell claims solubility = 0.00055, i.e., 1 part $SrCO_3$ in 18,045 parts of water.

[2] Advantage may be taken of the insolubility of strontium sulphate in ammonium sulphate in separating it from the soluble calcium salt.

The compounds of strontium are used for medicinal purposes; for red fire in pyrotechnics; for the manufacture of iridescent glass; the dioxide for bleaching purposes; the sulphide for luminous paint; the hydroxide for refining of beet-root sugar, being preferable to lime, as the saccharate of strontium is more granular.

dissolved in water and strontium determined by one of the procedures given later. See detailed procedure for separation under Barium.

**Separation of Strontium from Barium.** — The procedure is given in detail under chapter on Barium. In brief one of the following methods may be used: Strontium and barium in a mixture of the nitrates are separated from calcium by treatment with ether-alcohol mixture, in which $Ba(NO_3)_2$ and $Sr(NO_3)_2$ are insoluble. The nitrates dissolved in water are separated by precipitating barium as $BaCrO_4$ from a faintly acetic acid solution, strontium remaining in solution.

If preferred, barium may be first removed as a chromate, strontium and calcium precipitated from an ammoniacal solution by $(NH_4)_2CO_3$[1] as carbonates, the carbonates converted to nitrates and $Sr(NO_3)_2$ separated from $Ca(NO_3)_2$ in an ether-alcohol solution or by amyl alcohol. Details of the separations are given under Barium.

[1] N. B. Avoid a large excess of $(NH_4)_2CO_3$. $NH_4Cl$ has a solvent action on $SrCO_3$.

## GRAVIMETRIC METHODS

Strontium may be conveniently determined either as the sulphate, the carbonate or as the oxide. The first procedure is considered the best by authorities. The sample is brought into solution by a procedure given on the previous page.

### Determination as Strontium Sulphate, $SrSO_4$

**Procedure.** — A slight excess of dilute sulphuric acid is added to the neutral solution of strontium, and then an equal volume of alcohol. The mixture is stirred well and settled for several hours, or overnight, if more convenient. The precipitate, $SrSO_4$, is filtered onto a small ashless filter and washed first with 50% alcohol containing a little sulphuric acid, then with alcohol until free of acid. The precipitate is dried and the paper and the greater part of the salt ignited separately, then combined and weighed as $SrSO_4$.
Factors. $SrSO_4 \times 0.477 = Sr$, or $\times 0.8037 = SrCO_3$, or $\times 0.5642 = SrO$.

### Determination as Oxide, SrO

Strontium is precipitated as the oxalate by addition of ammonium oxalate to the slightly ammoniacal solution. The precipitate is filtered and washed with water containing ammonium oxalate. The residue is ignited and weighed as SrO.
Factors. $SrO \times 0.8456 = Sr$, or $\times 1.7726 = SrSO_4$, or $\times 1.4245 = SrCO_3$.

## VOLUMETRIC METHODS

The volumetric methods for determining strontium presuppose its isolation from other elements.

### Alkalimetric Method, Titration with Standard Acids

Either the carbonate or the oxide of strontium may be titrated with standard hydrochloric or nitric acids. The compound is treated with a known amount of standard acid added in excess, using methyl orange indicator. The solution is heated below boiling to complete the reaction and, upon cooling, the excess of acid is titrated with standard alkali.

One cc. of normal acid = 0.04381 gram of Sr, or 0.05181 gram of SrO, or 0.07381 gram of $SrCO_3$.

## SULPHUR

**S, at.wt. 32.07; sp.gr. 2.035; m.p. 111°; b.p. 444.53° C; oxides $S_2O_3$, $SO_2$, $SO_3$, $S_2O_7$; principal acids $H_2S_2O_4$, $H_2SO_3$, $H_2SO_4$, $H_2S_2O_3$, and $H_2S_2O'_8$.**

The determination of sulphur may be required in a great variety of substances, minerals, rocks, sulphur ores, acids, salts, water, gas, coal and other organic matter.

The substance occurs in nature principally in the following forms:

**Element.** — Found free, generally mixed with earthy matter. The commercial product is exceedingly pure and may contain over 99.5% of S.

**Sulphur Dioxide.** — The gas is found in volcanic regions.

**Hydrogen Sulphide.** — Occurs in mineral waters and in the air, from decaying organic matter.

**Sulphide Ores.** — Iron pyrites, $FeS_2$ (30 to 50% S); ferro ferric sulphide, $Fe_2O_3.5FeS$; pyrrhotite, $Fe_7S_8$; copper pyrites, $CuFeS_2$; realgar, $As_2S_2$; orpiment, $As_2S_3$; galena, PbS; cinnabar, HgS; zinc blende, ZnS.

**Sulphate Ores.** — Gypsum, $CaSO_4.2H_2O$, very abundant; barytes, or heavy spar, $BaSO_4$; celestite, $SrSO_4$; kieserite, $MgSO_4.H_2O$; bitter spar or Epsom salts, $MgSO_4.7H_2O$; Glauber salt, $Na_2SO_4.10H_2O$; sulphates of alkalies in animal and plant fluids.

The gravimetric determination of sulphur, by procedures of technical importance, depends upon its precipitation as barium sulphate, $BaSO_4$, after converting it into sulphuric acid, or a soluble sulphate, if not already in this form. Oxidation of free sulphur, sulphides, sulphites, metabisulphites, thiosulphates may be accomplished by either dry or by wet methods.

The volumetric methods of determining sulphur depend upon titration with oxidizing agents, or by acids, or by alkalies, according to the form of the sulphur compound, or by means of a substance forming an insoluble compound with sulphuric acid. For example sulphides are treated with a strong mineral acid (HCl). the evolved $H_2S$ absorbed in a suitable reagent, and the sulphide formed titrated with standard iodine. Sulphites may be determined either by oxidation with iodine or by titration with an acid in presence of methyl orange. Acid sulphites or metabisulphites may be determined by the iodine titration or by titration with an alkali in presence of phenolphthalein. Thiosulphates are titrated with iodine. Soluble sulphates may be titrated with standard barium chloride or chromate, added in slight excess, and the excess estimated by titration.

NOTE FOR STUDENTS. Sulphur is best determined gravimetrically. For practice it is advisable to start with a water soluble sulphate and follow directions under the first of the gravimetric procedures, page 542.

## DETECTION

The following tests include the detection of free sulphur and its more important combined forms.

**Element.** — Sulphur is a polymorphous, yellow, brittle, odorless and tasteless solid; existing in the rhombic, monoclinic and triclinic crystalline forms, and also in an amorphous state. At 111° it melts to a pale yellow liquid; at 180° it thickens to a dark gum-like material, containing a large percentage of amorphous sulphur; at 260° it becomes a liquid again, and at 444.53° it boils, giving off a brownish-red vapor.

*Heated in the air* sulphur burns with a blue flame, and is oxidized to $SO_2$, a gas with a characteristic pungent odor. This gas passed into a solution of potassium permanganate will decolorize it, if $SO_2$ is in excess of the amount that will react with the $KMnO_4$ in the solution.

If sulphur is dissolved in a hot alkali solution and a drop of this then placed on a silver coin, a stain of black $Ag_2S$ will be evident, due to the action of the sulphur.

**Sulphides.** — Hydrogen sulphide, $H_2S$, is liberated when a sulphide is treated with a mineral acid. This gas blackens moist lead acetate paper. $H_2S$ has a very disagreeable odor, which is characteristic.

**Sulphates.** — A white compound, $BaSO_4$, is precipitated in presence of free hydrochloric acid when a solution of barium chloride is added to a solution of a sulphate.

Insoluble sulphates are decomposed by boiling or fusion with alkali carbonates, forming water-soluble alkali sulphates.

**Sulphites.** — Sulphur dioxide, $SO_2$, is evolved when a sulphite is treated with hydrochloric acid. The odor of the gas is characteristic.

Sulphur dioxide decolorizes a solution of potassium permanganate. (Use very dilute solution.)

Sulphites are distinguished from sulphates by their failure to form a white precipitate when barium chloride is added to the solution acidified with hydrochloric acid; also by the fact that $H_2S$ is formed when zinc is added to a solution of a sulphite acidified by hydrochloric acid.

**Thiosulphates.** — Sulphur dioxide is evolved and free sulphur precipitated when a thiosulphate is acidified with dilute mineral acids. In presence of oxidizing agents sulphides will also liberate free sulphur.

Thiosulphates are strong reducing agents

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

In the preparation of the sample the following facts regarding solubility of sulphur and its combination should be kept in mind.

**Element.** — The crystalline forms are soluble in $CS_2$, the monoclinic form is soluble also in alcohol, chloroform and benzol. Yellow amorphous and plastic sulphur are insoluble in $CS_2$. Sulphur precipitated by the action of HCl upon $(NH_4)_2S_x$ is soluble in benzol. The element is soluble in hot hydrates of sodium, potassium, barium and calcium, forming polysulphides and thiosulphates.

**Sulphide.** — Sulphides of Na, K, Cs, Rb, Ca, Sr, Ba, Mg, Mn, Fe are soluble in dilute mineral acids. The sulphides of Ag, Hg, Pb, Cu, Bi, Cd, Co, Ni require strong acids for decomposition. These are also insoluble in sodium hydroxide and potassium hydroxide solutions. As, Sb and Sn sulphides are insoluble in dilute acids, but soluble in alkalies.

**Sulphate.** — With exception of $BaSO_4$, $CaSO_4$, $SrSO_4$ and $PbSO_4$, sulphates are soluble in water.

**Thiosulphate.** — Nearly all are soluble in water.

**Sulphite.** — With exception of the sulphites of the alkalies, sulphites of the metals are difficultly soluble in water, but readily decomposed by acids.

### Decomposition of Sulphur Ores

The wet procedure for oxidation and decomposition of sulphur ores given in detail under the Gravimetric Methods is applicable to a wide range of substances.

**Fusion Method.** — One gram of the finely ground ore (80 mesh) is intimately mixed with 6 grams of zinc oxide-sodium carbonate mixture (4 parts of $ZnO$ + 1 part of $Na_2CO_3$), placing 2 grams more of the mixture over the charge. The material is fused and sulphur extracted according to the procedure described for coal — Eschka's method.

Weigh 0.5 gram of the finely ground ore into a small spun-iron crucible of about 25 cc. capacity. Add 1 gram of dry sodium carbonate and about 5 grams of sodium peroxide (calorimeter quality) and mix well with a spatula or glass rod. Place the crucible in a hole cut in asbestos board (to avoid sulphur in gas) and fuse at a gentle heat over a Bunsen burner. Heat slowly, only to dull red, or the crucible will be strongly attacked. Agitate occasionally to complete fluidity. Allow to cool until mass is just solid.

While still hot, set the crucible in about half an inch of cold water contained in a 400 cc. beaker. Cover the beaker and upset the crucible with a glass rod. The contents will quickly disintegrate.

Rinse off beaker cover and remove and wash crucible. Add about 5 grams of solid ammonium carbonate to partially destroy the causticity of the peroxide, warm gently until dissolved and then filter, best by using a perforated porcelain filter-plate and suction. Wash ten times with hot water. Receive filtrate in a 500 cc. Erlenmeyer flask having a mark at the 300 cc. point. If the filtrate is greenish, indicating manganese, it is a good plan to add 5 cc. of alcohol, boil and filter again.

Add a few drops of methyl orange as indicator, make just acid with HCl and then add 0.9 cc. of the strong acid in excess.

Dilute to 300 cc. with hot water, heat to boiling and then add an excess of a 10% Barium chloride solution, through a small funnel which has the stem drawn down to an aperture that will deliver 10 cc. in about 3 minutes. Ten cc. of a 10% barium chloride solution will precipitate about 0.13 gram of sulphur.

### Sulphur in Rocks, Silicates and Insoluble Sulphates

The material in finely powdered form is fused in a large platinum crucible with about six times its weight of sodium carbonate (sulphur free) mixed with about 0.5 gram of potassium nitrate. The charge is protected from the flame by an asbestos board or silica plate with an opening to accommodate the crucible snugly. The fusion is extracted with water, the filtrate evaporated to dryness and silica dehydrated. The residue is moistened with strong hydrochloric acid, then taken up with a little water, boiled free of $CO_2$, and silica filtered off. The filtrate contains the sulphate, which now is precipitated as barium sulphate according to one of the standard procedures.

**Barium Sulphate.** — This is transposed by fusion with sodium carbonate, as stated above. Barium carbonate remains in the water-insoluble residue. It is advisable to wash the residue in this case with hot sodium carbonate solution, to insure complete removal of the sodium sulphate. The filtrate is acidified with HCl, boiled free of $CO_2$ and $BaSO_4$, then precipitated.

**Lead Sulphate.** — This may be transposed by digesting the compound with a strong solution of sodium carbonate saturated with $CO_2$, keeping the solution at boiling temperature for half an hour or more. The sulphate will be in solution and the lead is precipitated as the water-insoluble carbonate.

Strontium or calcium sulphates may be transposed by the procedure described for lead.

### Sulphur in Coal, Eschka's Method

One gram of coal is intimately mixed with 3 grams of Eschka's compound, consisting of 2 parts of porous, calcined magnesia and 1 part of anhydrous sodium carbonate. The mixture, placed in a platinum crucible, is covered with about 2 grams more of Eschka's com-

pound. The charge is placed in an open platinum crucible, which is protected from the flame by a shield, as shown in Fig. 110. If possible, a sulphur-free flame should be used to avoid contaminating the material. With proper precautions, the shield will prevent this. Heating in a crucible electric furnace completely avoids sulphur contamination. The mixture is heated very gradually, to drive off the volatile matter, the charge being stirred frequently with a platinum wire to allow free access of air. The heat is increased, after half an hour, to a dull redness. When the carbon has burned out, the gray color having changed to a yellow or light brown, the heat is removed and the crucible cooled.

The powdered fusion is digested with 100 cc. of hot water for half an hour, and the clear liquor decanted through a filter into a beaker. The residue is washed twice more with hot water, by decantation, and finally on the filter, until the volume of the total filtrate amounts to about 200 cc. About 5 cc. of bromine and a little hydrochloric acid are added, and the solution boiled. Sulphuric acid is now precipitated as $BaSO_4$ by addition of barium chloride to the hot solution, and sulphur determined by the first of the gravimetric procedures.

**Water Soluble Sulphate Salts.** — Weigh 1–2 grams of the salt and place in a 500–600 cc. beaker. (If preferred a factor weight of 2.058 grams may be taken. The $BaSO_4$ precipitate multiplied by 20 will give the per cent for this amount of sample.)

Dissolve in distilled water and dilute to 300 cc. If the solution is neutral (methyl orange indicator) add 1 cc. of strong HCl. The solution should contain about 0.3 cc. free HCl per 100 cc. Precipitate the $BaSO_4$ as directed in the first gravimetric procedure.

### Substances Containing Iron

In precipitating barium sulphate, in presence of ferric salts, from hot solutions by the gravimetric procedure commonly followed, considerable iron is carried down by the precipitate. Since $Fe_2(SO_4)_3$ loses $SO_3$ upon ignition, and since $Fe_2O_3$ weighs much less than $BaSO_4$, low results will be obtained. Hence the removal of iron is necessary, or a method should be followed in which iron does not interfere. It is found that barium sulphate precipitated from a large volume of cold solution, in which the iron has been reduced to ferrous condition, is free from iron.

If sulphur is to be precipitated from hot solution of comparatively small volume (200 to 400 cc.), it is necessary to remove iron. This is accomplished by precipitating this as $Fe(OH)_3$ by addition of ammonium hydroxide in decided excess (5 to 10 cc excess of strong $NH_4OH$, sp.gr. 0.90). If the solution is barely neutralized with ammonia, the iron hydroxide carries down considerable of the sulphate. Even with the precaution recommended some of the combined sul-

phuric acid is occluded by the precipitate, so that it is necessary to recover this by dissolving the precipitate with hydrochloric acid and reprecipitating the ferric hydroxide with an excess of ammonia. The combined filtrates are now treated with barium chloride, upon acidification with hydrochloric acid, according to the gravimetric procedure first given.

### Separation of Sulphur from Metals Forming an Insoluble Sulphate

This is accomplished by fusion of the compound with sodium carbonate and extraction of the mass with water. The metal remains with the residue and the sulphate of the alkali passes into solution.

**Nitrates and Chlorates.** — These are carried down with the precipitate as barium salts if they are present in appreciable amount. They may be removed from the solution by evaporation to dryness with hydrochloric acid.

**Silica.** — Silica will be carried down with the barium sulphate precipitate if present in appreciable amounts. It is removed by evaporation of the solution with hydrochloric acid, dehydrating the silicic acid, taking up with HCl and water and filtering.

**Ammonium and Alkali Salts.** — These have a negligible effect on the precipitate of $BaSO_4$ if this is precipitated from a large volume, according to the second gravimetric procedure.

## GRAVIMETRIC DETERMINATION OF SULPHUR

### PRECIPITATION AS BARIUM SULPHATE

**Preliminary Remarks.** — The procedure depends upon the insolubility of barium sulphate, $BaSO_4$, in neutral or slightly acid solutions. It was formerly the general practice to precipitate the sulphur by adding a 10% barium chloride solution to the hot sulphate solution, which had been diluted from 100 to 400 cc., according to the amount of sulphur that was present (not over 0.2 gram of sulphur per 100 cc.), containing 1 to 3 cc. of free concentrated hydrochloric acid per 100 cc. of solution. Special precautions were given to have the solution boiling hot, and to avoid having a volume of over 400 cc., a smaller sample being taken in high sulphur ores, rather than increase the volume. Extended experiments have shown that it is preferable to precipitate the sulphate from a large volume of cold solution. The product obtained is less apt to occlude impurities, the crystals are larger than those obtained in hot concentrated solutions, and do not pass through the filter. Precipitation may be made in presence of large amounts of iron, copper and other impurities. The procedure requires large beakers of 2- to $2\frac{1}{2}$-liter capacity, special precipitating cups, and a suction apparatus, as shown in Figs. 105 to 107. This apparatus may not always be available, and occasionally it is advantageous to precipitate the sulphur in a small volume, especially when the sulphur content of the material is low, hence, although the second procedure is generally recommended, the older method is also included.

#### I. Precipitation of Sulphur as Barium Sulphate, from Hot Solutions

By this method the sulphate radical is precipitated from hot solutions of comparatively small volume by adding barium chloride in solution, the following reaction taking place:

$$M_2SO_4 + BaCl_2 = 2M.Cl + BaSO_4 \quad (M = \text{an univalent element})$$

**Reagents.** *Barium Chloride.* — 10% solution. If the crystal salt, $BaCl_2.2H_2O$, is used, 1 cc. of this solution is equivalent to 0.013 gram of sulphur or to 0.039 gram of $SO_4$. With the anhydrous salt approximately 1.18 times these amounts.

*Hydrochloric Acid.* — Strong HCL. (sp.gr. 1.2)

**Procedure.** 1. *Solution.* — The sample having been brought into solution by a suitable procedure given under Preparation and Solution of the Sample, and having been diluted to a volume of about 300 cc. after being neutralized (in presence of methyl orange indicator or litmus) and then acidified with hydrochloric acid, 0.33 cc. HCl per 100 cc. of solution, proceed as follows:

2. Heat the solution to boiling and add by means of a burette or precipitating cup or funnel with a capillary tube, at the rate of about 3 cc. per minute, sufficient of the 10% barium chloride reagent to precipitate the $SO_4$ and then about 10 cc. excess. 20 cc. of the reagent per gram of sample taken, should be sufficient if a salt is examined, a larger amount is necessary for sulphur ores. See procedure 2.

3. Boil for about five minutes after the reagent is added. Remove from the flame and allow to cool and settle.

4. Decant the clear solution into a filter (11 cm. fine mesh) or into a weighed Gooch crucible. Wash twice by decantation with hot water, then transfer the precipitate by means of a stream of hot water to the filter, using a stirring rod, held by the forefinger over the beaker, to guide the precipitate. Wash the precipitate six times in the filter, directing a fine stream of hot water from the wash bottle around the upper portion of the filter, filling the filter about $\frac{2}{3}$ full at each washing. Test the first portion of the washing for $SO_4$ to insure complete precipitation.

5. If a filter paper has been used pinch the filter together at the top and invert with apex pointing up in a weighed crucible. Now place the crucible or the Gooch with the precipitate, on a hot plate or sand-bath dish over a free flame for about five minutes. Then place over a free flame and ignite until the filter paper is completely burned and the residue is a pure white.

Note 1. If much iron or aluminum is present it is advisable to precipitate the sulphate from a large volume, by the second method, rather than to attempt to remove these substances. If $BaSO_4$ is present in the original material its weight should be included with that of the precipitate.

Note 2. If the residue appears yellow or red, contamination with iron is indicated. The barium sulphate absorbs or occludes iron as ferric sulphate if this is present, hence it should be removed if this procedure is followed. Ferric sulphate decomposes with heat with liberation of $SO_3$ so that the results will be low if the contamination has occurred.

6. Weigh the crucible with the precipitate. Deduct the weight of the crucible and calculate the weight of the sulphur or sulphur oxide, as desired, from the weight of the barium sulphate obtained.

**Factors.** $BaSO_4 \times 0.1373 = S$, or $\times 0.4202 = H_2SO_4$, or $\times 0.3766 = FeS$, or $\times 0.2744 = SO_2$, or $\times 0.3430 = SO_3$, or $\times 0.4115 = SO_4$.

### II. Precipitation of Barium Sulphate from Cold Solutions — Large Volume [1]

**Introduction.** — The method is especially adapted to the determination of sulphur in iron pyrites and materials high in sulphur, 30 to 50% of sulphur, but by varying the amount of material used the range may be extended. The finely ground sample is oxidized by means of a mixture of bromine and potassium bromide, followed by nitric acid. The nitric acid is expelled by evaporation to dryness, followed by a second evaporation with hydrochloric acid, which dehydrates the silica. Iron is now reduced to the ferrous condition and the silica and residue, undissolved by addition of hot water and HCl, is filtered off. The sulphur is precipitated in a large volume of cold solution, by barium chloride solution, as $BaSO_4$ and so weighed.

**Reagents.** *Bromine — Potassium Bromide Solution.* — 320 grams of potassium bromide are dissolved in just sufficient water to cause solution and mixed with 200 cc. of bromine, the bromine being poured into the saturated bromide solution. After mixing well the solution is diluted to 2000 cc.

*Bromine — Carbon Tetrachloride Solution.* — Carbon tetrachloride saturated with bromine.

*Barium Chloride,* anhydrous, 5% solution; or crystals, 6% solution.

**Procedure.** *Preparation of Sample.* — The sample ground to pass 80 mesh sieve is carefully mixed and quartered down to 10 grams. This is dried for one hour at 100° C. and then placed in a weighing tube.

A factor weight, 1.3733 grams of the sample, is placed in a deep beaker, 300 cc. capacity, $2\frac{1}{2}$ by $4\frac{1}{2}$ ins.

*Oxidation of Sulphur.* — Ten cc. of the bromine-potassium bromide mixture for pyrrhotite ore, or bromine — carbon tetrachloride reagent for pyrites ores, are added and the beaker covered with a dry watch-glass cover. After standing fifteen minutes in the cold bath (a casserole of water will do), with occasional shaking of the beaker, 15 cc. of strong nitric acid are added and the mixture allowed to stand fifteen minutes longer, at room temperature, and then warmed on an asbestos board on the steam bath until the reaction has apparently ceased and the bromine has been volatilized. The beaker is now placed within the ring of the steam bath so that the lower portion is ex-

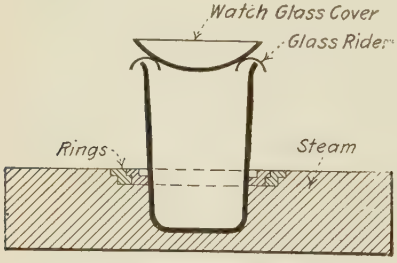


Fig. 106.

[1] Standard method of the General Chemical Company.

posed to steam heat. The solution is evaporated to dryness, the cover of the beaker being raised above the rim by means of riders (U-shaped glass rods), Fig. 106; 10 cc. of strong hydrochloric acid are now added and the solution again evaporated to dryness to expel the nitric acid. The silica is dehydrated by heating in the air oven at 100° C. for one hour, or overnight if preferred.

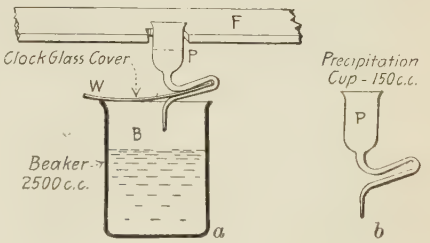



Fig. 107. Apparatus for Precipitating Sulphur.

*Reduction of Iron.* — Four cc. of hydrochloric acid (sp.gr. 1.20), followed five minutes later by 100 cc. of hot water, are added, the sides of the beaker and the cover being rinsed into the solution. The riders being removed, the sample is gently boiled for five minutes to insure the solution of the sulphate. After cooling for about five minutes, approximately 0.2 gram of powdered aluminum is stirred into the solution, keeping covered during the intervals between stirring. When the iron has been reduced, the solution becoming colorless, the sample is filtered into a 2500 cc. beaker, through a fine-grained 12½ cm. filter paper. The beaker should be copped out and the residue on the filter washed nine times with hot water, filling the filter funnel and draining each time.

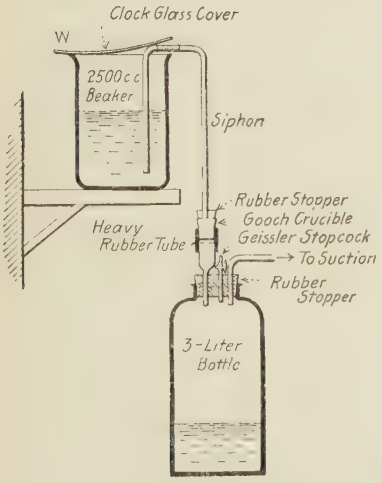



Fig. 108. Apparatus for Filtering Barium Sulphate.

*Precipitation of the Sulphur.* — The solution in the large beaker is diluted to 1600 cc. with cold water and 6 cc. of HCl (sp.gr. 1.20) added, and mixed by stirring. The barium chloride solution is now added by means of a special delivering cup (Figs. 107, 108), which should drain at the rate of 5 cc. per minute. 125 cc. of barium chloride solution are added for ores containing 30 to 50% of sulphur, the factor weight being taken. The solution is not stirred while the barium chloride is being added, but when the cup has drained, the solution is mixed by stirring. The $BaSO_4$ is allowed to settle, two or three hours being advisable, overnight being preferred.

*Filtration.* — The clear solution is filtered through a weighed Gooch crucible (35 cc.), using suction. This is best done by the

automatic arrangement shown in Fig. 108. The beaker containing the solution is placed on a shelf; a siphon dipping to within half an inch of the precipitate at the bottom of the beaker is connected to the Gooch crucible by means of a tightly fitting stopper. The Gooch and thistle tube are best connected by heavy rubber tubing. The suction flask, or bottle, should have a capacity of about 3 liters. A Geissler stop-cock passes through the rubber stopper in the suction flask to relieve the pressure when the Gooch is to be removed. The precipitate is washed onto the asbestos mat in the crucible and washed with cold water six times, the beaker being copped out as usual.

*Ignition.* — The precipitate is dried by placing the crucible on an asbestos board over a flame for twenty-five minutes and then heated over a direct flame for thirty minutes.

**Calculation.** $BaSO_4 \times 10$ = per cent of S. (If factor weight is taken.)

Factor. $BaSO_4 \times 0.1373$ = gram of S.

### Notes and Precautions

Although barium sulphate is only slightly soluble in water, it is appreciably soluble in the salts of the alkalies (Na, K and $NH_4$), and in a large excess of hydrochloric acid.

Barium sulphate occludes salts, especially nitrates and chlorides. Ferric chloride is carried down with this precipitate, though ferrous chloride is not; hence the reduction of iron is necessary. Occlusion of iron causes low results, as will be seen from the fact that with heating of $Fe_2(SO_4)_3$, $SO_3$ is volatilized, the salt decomposing to $Fe_2O_3 + SO_4$. With the iron reduced the precipitate burns perfectly white, whereas with ferric iron present the precipitate is invariably red or yellow.

## EVOLUTION METHOD FOR DETERMINING SULPHUR IN IRON, STEEL, CINDERS, SULPHIDES AND METALLURGICAL PRODUCTS

**Introduction.** — The method depends upon the fact that hydrogen sulphide is evolved when a sulphide is acted upon by a strong acid such as hydrochloric acid. This gas, absorbed by a suitable reagent, may be determined volumetrically [1] by titrating the precipitated sulphide with iodine or by titrating the acid, formed by the reaction, with standard caustic. The iodine and caustic titrations may be made on the same run, or the sulphide may be weighed and the filtrate containing the free acid titrated, thus double checking results. The following reaction takes place when the gas is evolved and absorbed by neutral cadmium sulphate:

$$H_2S + CdSO_4 = CdS \text{ precipitate} + H_2SO_4 \text{ free acid.}$$

The method is especially adapted to the determination of sulphur in iron and steel or in metallurgical products containing small amounts of sulphide. It may be applied to products containing larger amounts of sulphur as sulphides or sulphates, the latter condition requiring a special preliminary treatment.

The method is not applicable for determining free sulphur or sulphur in iron pyrites.

**Reagents.** *Iodine Solution.* — Two strengths of this reagent should be at hand for general work:

For iron and steel and low sulphur briquettes, etc., = .01 to 0.5% S. . . . . N/30 I

For sulphur products containing over 0.5% S. . . . . N/10 I

*Starch Solution.* — Made from a good grade of soluble starch, 1 gram per 200 cc. of water. Fresh solutions are desirable, as the deteriorated material produces a greenish-brown color in place of the delicate blue desired. Flecks of insoluble starch will cause the same difficulty.

*Cadmium Chloride or Cadmium Sulphate Solutions. Ammoniacal Solution.*— Fifty-five grams of $CdCl_2.2H_2O$ or 70 grams of the sulphate are dissolved in 500 cc. of distilled water. To this are added 1200 cc. of $NH_4OH$ (sp.gr. 0.90) and the solution diluted to 2500 cc. The solution is of such strength that 50 cc. will precipitate approximately 0.175 gram of sulphur evolved as $H_2S$. This is equivalent to about 3.5% of sulphur on a 5 gram sample.

*Neutral Solution.* — To be used where titration with caustic is desired. Seventy grams of $CdSO_4$ are dissolved in water and made up to 2500 cc. The solution should be neutral to methyl orange, otherwise add the requisite amount of $H_2SO_4$ or NaOH necessary, determined by titration of an aliquot portion.

[1] *Volumetrically.* (*a*) Absorption in a solution of KOH, $CdCl_2$ or $CdSO_4$, $ZnCl_2$ or $ZnSO_4$, $Na_2HAsO_3$ and titration with iodine solution. (*b*) Absorption in iodized KI and titration of the excess of iodine with $Na_2S_2O_3$ solution.

*Hydrochloric Acid.* — One part of concentrated acid to an equal volume of distilled water.

*Sulphuric Acid.* — One volume of concentrated acid to four volumes of distilled water.

*Reducing Mixture for Reduction of Sulphates.* — Five parts of $NaHCO_3$, 2 parts of C.P. aluminum powder and 1 part of pure carbon, best made by charring starch. A blank should be determined on this material and allowance made accordingly.

*Stannous Chloride.* — Ten per cent solution.

*Fine Granular Aluminum or Zinc Metal.* — Sulphur free, 20 mesh.

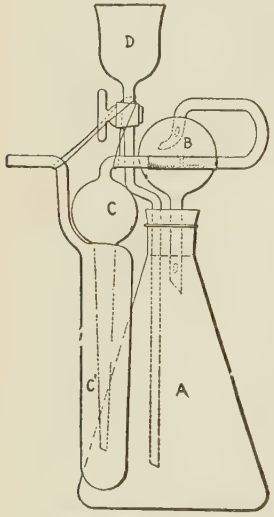



FIG. 109. Scott's Apparatus for Determining Sulphur in Iron and Steel.

**Apparatus.** — The apparatus shown in the illustration, Fig. 109, is the author's [1] modification of the form used at Baldwin Locomotive Works. This consists of an Erlenmeyer flask *A* of about 500 cc. capacity with large base. With material in which violent foaming occurs, during the evolution of hydrogen sulphide, it is advisable to use a wash bottle with large base, in preference to an Erlenmeyer flask. Through a rubber stopper is inserted a thistle tube with glass stop-cock *D*, by which the acid is introduced into the flask. The hydrogen sulphide passes through a potash connecting bulb with trap as shown. A hole blown in the side of the tube prevents liquid being swept through. Connected to the potash bulb is the absorption bulb *C*, which is suspended by a wire attached to the thistle tube. The apparatus is compact, so that on a large hot plate, 30 by 20 ins., a dozen outfits may readily be accommodated. With the use of this apparatus the writer has been able to make over seventy-five determinations of sulphur in steel in an ordinary day's run.

### Preparation and Amount of Sample

The amount of material to be taken for the determination depends upon the sulphur content as shown by the following table:

| Approximate % of Sulphur Present. | Amount to take for Analysis. |
|---|---|
| 0.01 to 1 | 5 grams |
| 1.0 to 10 | 1 |
| 10.00 to 30 | 0.5 |
| Above 30 | 0.25 |

The class of material will govern the method of procedure.

[1] W. W. Scott.

**Iron and Steel.** — A 5 gram sample of drillings or finely divided material is treated directly in the evolution flask with hydrochloric acid, 1: 1, and the hydrogen sulphide absorbed in ammoniacal cadmium chloride. The sulphide formed is titrated with iodine.

**Iron Ore Briquettes and Materials Containing Sulphates. — Low Sulphur.** *Preliminary Reduction.* — A 5 gram sample is intimately mixed with an equal weight of reducing mixture ($NaHCO_3 + Al + C$) and wrapped in a 9 cm. ashless filter. The charge is placed in a 50 cc. nickel crucible with cover. The crucible is inserted half way into an asbestos board or perforated silica plate (see Fig. 110) and after covering, placed over a low flame of a Meker blast burner. The flame of the blast is gradually increased during the first five minutes and the charge blasted for about twenty minutes. The crucible will appear a bright red and carbon monoxide gas escaping from under the crucible lid will burn. The loss of sulphur, however, is not appreciable. The crucible is cooled without removing the cover. When cold the fused mass is quickly pulverized and placed in the dry evolution flask containing a mat of aluminum granules or C. P. zinc dust or granulated tin. Hydrogen sulphide is best evolved with hydrochloric acid to which 4 or 5 cc. of 10% stannous chloride has been added to reduce ferric iron. The gas is absorbed in ammoniacal cadmium chloride and the cadmium sulphide formed titrated with iodine.

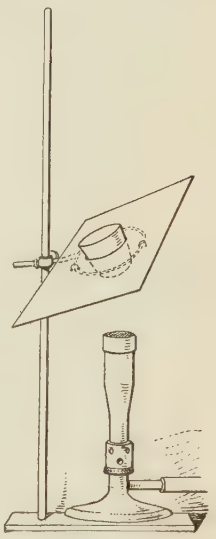


Fig. 110.

**Iron Sulphide for Available $H_2S$.** — Since this product runs over 20% available hydrogen sulphide not over 0.5 gram sample should be taken. The $H_2S$ is evolved by addition of dilute sulphuric acid, 1 : 4, in place of hydrochloric acid, and is absorbed by neutral cadmium sulphate. The acid formed by the reaction is titrated by standard N/10 NaOH.

**Sodium Sulphide or Water-Soluble Sulphides for Available $H_2S$.** — Ten grams dissolved in water and diluted to 1000 cc.; 50 cc. = 0.5 gram taken for analysis.

### Details of Procedure

*Evolution of Hydrogen Sulphide.* — One-half to 1 gram of aluminum or zinc granules, 20 mesh, is placed over the bottom of the evolution flask and the sample placed above this mat of metal. The stopper with the thistle tube and condenser is inserted snugly into the neck of the flask. An absorption bulb containing about 20 cc. of distilled water is attached to the condenser. This bulb serves as a trap for the HCl that is driven out of the flask during the boiling. To this bulb is attached a second bulb containing 50 cc. of am-

moniacal cadmium chloride. A third bulb may be attached if the sulphur content of the material examined is high; this, however, is seldom necessary when ammoniacal cadmium chloride is used. The rubber stopper and all rubber connections being air-tight, 100 cc. of warm HCl, 1 : 1, is poured into the flask through the thistle tube, the stem of which should now dip well below the acid. The stopcock is closed during the violent action of the acid on the sample and opened when this has subsided. The acid trap prevents loss of $H_2S$ through the thistle tube. The apparatus is now placed on the hot plate and the sample boiled vigorously for about twenty minutes. The flask is taken off the hot plate and the contents allowed to cool. At this stage it may be advisable to draw a current of air through the apparatus to sweep out any residual $H_2S$ that may remain in the flask. Hydrogen gas is preferable to air.

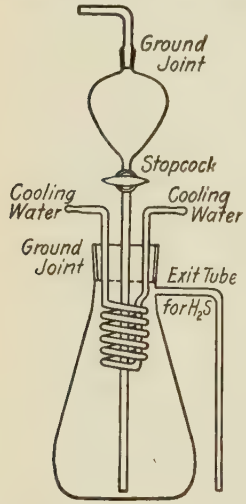



FIG. 110a. A New Standard Apparatus for the Determination of Sulphur in Iron and Steel by the Evolution Method.

Courtesy of Schaar & Co., Chicago.

*Titration.* — (*a*) The contents of the bulbs are poured into a 600 cc. beaker containing about 400 cc. of distilled water. The bulbs are washed out first with water and then with dilute acid. The excess of ammonia is neutralized with concentrated HCl, 5 cc. of starch solution added and the sulphide immediately titrated with standard iodine, additional hydrochloric acid being added from time to time during the titration to insure complete decomposition of the sulphide. The liquid appears yellowish red, orange, purplish red and finally a deep blue. Since the sulphide, when present in appreciable quantity, decomposes slowly, the solution should be strongly acid at the completion of the titration, and five minutes should be allowed for a permanent end-point.

Knowing the amount of iodine necessary, a check run may be made by adding to the neutral solution an excess of iodine followed by 5 cc. of starch solution and a large excess of concentrated hydrochloric acid. The excess of iodine is titrated with N/10 thiosulphate, $Na_2S_2O_3$, solution. (Arsenous acid will not do.) This procedure will prevent the loss of $H_2S$, which is apt to occur in samples high in sulphide.

(*b*) *An alternate method* is frequently advisable in high sulphurs. The precipitate is separated from the solution containing ammonia by filtration. The cadmium sulphide is now placed in the 600 cc. beaker with water and an excess of iodine run in. Starch is added, followed by hydrochloric acid. The excess of iodine is titrated with sodium thiosulphate, $Na_2S_2O_3$. By this method the heat action during the neutralization of ammonia is avoided and only the precipitate is titrated.

When the iodine titration exceeds 50 cc. of N/10 iodine, a smaller amount of the sample should be taken for analysis; the iodine titration for amounts of sulphur exceeding 0.1 gram is not satisfactory, owing to a fading end-point. The method for determining available hydrogen sulphide in high sulphide products, dealing with the titration of the free acid formed during the reaction, permits of larger samples being taken. Details of this method are given on page 549.

One cc. of N/10 iodine = 0.001604 gram S.

*Tenth Normal Equivalents*

| | | |
|---|---|---|
| One cc. of N/10 iodine | = 0.008471 | gram of BaS |
| " " | = 0.003607 | gram of CaS |
| " " | = 0.007224 | gram of CdS |
| " " | = 0.004782 | gram of CuS |
| " " | = 0.004396 | gram of FeS |
| " " | = 0.011634 | gram of HgS |
| " " | = 0.001704 | gram of $H_2S$ |
| " " | = 0.003904 | gram of $Na_2S$ |
| " " | = 0.011959 | gram of PbS |
| " " | = 0.00561 | gram of $Sb_2S_3$ |
| " " | = 0.004872 | gram of ZnS |

## DETERMINATION OF FREE SULPHUR IN A MIXTURE

From 1 to 10 grams of the material, depending upon the amount of sulphur present, is extracted in a Soxhlet extractor (see modified form Fig. 111) with carbon tetrachloride, or carbon bisulphide (freshly distilled) for twelve hours. The extract is evaporated to dryness, adding 10 cc. of bromine-carbon tetrachloride mixture together with 15 cc. of nitric acid. The residue is taken up with 10 cc. of hydrochloric acid, diluted with 150 cc. of distilled water, heated to boiling and the sulphuric acid precipitated with 10% barium chloride solution, washed, dried, ignited and weighed according to the procedure for sulphur.

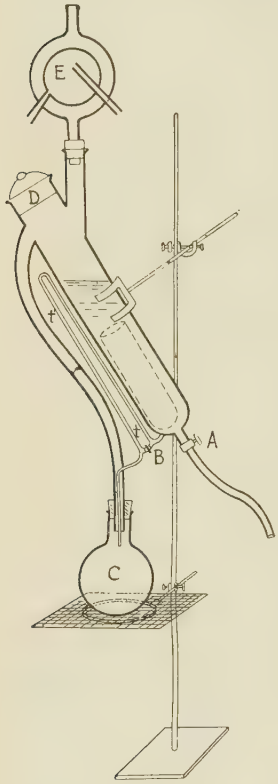



Fig. 111. Sanders' Extraction Apparatus.

$$\frac{BaSO_4 \times 100 \times 0.1373}{\text{Weight of sample}} = \text{per cent of free sulphur.}$$

Sanders' extraction apparatus [1] has several advantages that make this apparatus desirable for laboratory use, where a number of daily extractions are required. As may be seen from Fig. 110, by simply removing the glass stopper *D* the cylinder may be charged without disconnecting the apparatus, as is necessary with the Soxhlet type of apparatus. The extraction is carried on with the traps *A* and *B* closed, the siphon *t*–*t'*, acting automatically as in case of the Soxhlet. With *A* closed and *B* open the apparatus may be used as a reflux condenser. The solvent liquid may be drawn off by opening *A*. With *B* closed and *A* open the apparatus may be used as a condenser and the ether, chloroform, carbon disulphide, etc., distilled from *C*. The globe-shaped Soxhlet condenser may be replaced by Allihn's or Liebig's condenser, if desired. The ball form, however, is more compact.

[1] J. McC. Sanders, Proc. Chem. Soc., 26, 227–228, 1910. The Analyst, 35, 556, 1910.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### Analysis of Brimstone

The impurities in brimstone are seldom more than a few tenths per cent. In the usual analysis, moisture, available sulphur, ash, arsenic, and chlorine are required.

**Moisture.** — The powdered sample, weighing 50 grams, is spread out on a watch-glass and dried for an hour at 100° C., then cooled in a desiccator and weighed.

Loss of weight in grams multiplied by 2 = per cent moisture.

**Available Sulphur.** — Ten grams of the sulphur taken from the dried material are heated in a silica or porcelain dish until the sulphur ignites. The heating is discontinued during the burning of the substance, but renewed for a minute or so after the sulphur has burned away. Loss of weight of the cooled residue is due to the available sulphur.

NOTE. Organic matter in brimstone is not appreciable.

**Ash.** — This is the residue that remains in the dish. The increase of weight of the tared dish is due to the ash.

**Arsenic.** — Ten grams of the material are treated with 30 cc. of carbon tetrachloride mixture (3 parts of $CCl_4$ : 2 parts of Br) and after standing for ten minutes 25 cc. of strong nitric acid are added in small portions (a watch-glass covering the beaker during the intervals of addition). $CCl_4$, $HNO_3$ and Br are expelled by evaporation on the steam bath. Water is added and the evaporation repeated. Arsenic is now determined on the residue by the Gutzeit Method for arsenic.

NOTE. A. H. Low adds to the $CCl_4$ solution 50 cc. of dilute $NH_4OH$ (1 : 43), and evaporates off $CCl_4$ on a hot water bath. The solution is filtered from precipitated sulphur, 1 gram of $Na_2CO_3$ added and $NH_3$ expelled by boiling. 3 grams of $Na_2SO_4$ and 5 cc. of $H_2SO_4$ added, and the mix heated until the product is reduced to a molten mass. The cake is treated with 50 cc. of hot water and heated until in solution. Arsenic is now titrated by the iodine method, using about $\frac{1}{5}$ the usual strength of iodine solution.

NOTE. Arsenic-free reagents should be employed.

**Chlorine.** — One hundred grams of the brimstone are extracted with hot water, the filtered extracts oxidized with 10 to 15 cc. of nitric acid and a few crystals of ammonium persulphate by boiling and treated with 5 cc. of 10% solution of silver nitrate. The solution, brought to boiling, is placed in a dark place and the silver chloride allowed to settle. This is now filtered off in a weighed Gooch crucible and chlorine calculated from the AgCl.

$$AgCl \times 0.2474 = Cl \text{ or } \times 0.4078 = NaCl.$$

**Total Sulphur.** — This is best determined by oxidation of the free sulphur to sulphuric acid by treating with bromine, followed by nitric acid. Sulphuric acid is now determined gravimetrically by precipitation as $BaSO_4$.

## SULPHURIC ACID GASES

### Burner Gases. Sulphur Dioxide

This gas may be determined by the method of Reich. It consists in aspirating the gas through standard iodine solution (N/10 is suitable) until it is decolorized. The amount of iodine used in the test and the volume of the aspirated gas being known, the percentage of $SO_2$ can readily be calculated.

Fig. 112 shows a form of apparatus for making this determination. The standard iodine, 5 to 25 cc. N/10 I, diluted to 150 to 200 cc.,

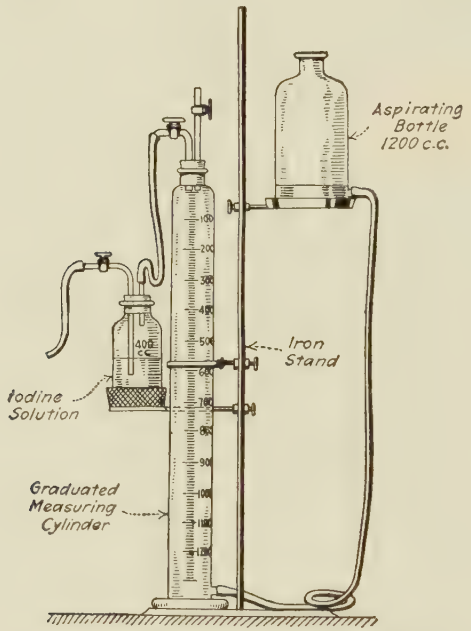



Fig. 112. Portable Reich Apparatus.

is placed in the bottle, about 400 cc. capacity, and starch indicator added. The gas to be tested is aspirated through the iodine until the color of the starch blue fades completely. Water which flows out from the graduated cylinder by lowering the aspirating bottle, produces the suction, and the amount measures the volume of the aspirated gas. From the quantity of iodine used and the volume of the gas required to decolorize the solution the per cent of sulphur dioxide is calculated.

Should the contact gas contain $SO_3$, this is absorbed by passing the gas through 50 to 100 cc. of strong $H_2SO_4$, to avoid the action of $SO_3$ on the rubber tubing of the apparatus. A rapid current of the gas is passed through the acid to saturate it with $SO_2$ before making the tests.

The Reich method is more applicable for determining small amounts of $SO_2$. A 12–15 liter graduated aspirating bottle is used in works tests of exit gases for measuring the gas. Since these volumes are under standard conditions (760 mm. and 0° C.), it will be necessary to convert the volumes obtained in the tests to these conditions, using the formula

$$V = V^\circ \frac{P^\circ - w}{760\ (1+10.00367t)},$$ where $V^\circ$ = measured volume, $P^\circ$ = observed barometric pressure, $t$ = temperature of the gas, and $w$ = aqueous vapor pressure at temperature of the test.

TABLE FOR REICH'S TESTS FOR PERCENTAGE $SO_2$. USING TENTH NORMAL IODINE SOLUTION

| Volume Per cent $SO_2$ | 25 cc. N/10 Iodine | 10 cc. N/10 Iodine | 5 cc. N/10 Iodine |
|---|---|---|---|
| 12 | 205 cc. gas | ..... | ..... |
| 11.5 | 215 " " | ..... | ..... |
| 11 | 226 " " | ..... | ..... |
| 10.5 | 238 " " | ..... | ..... |
| 10 | 252 " " | ..... | ..... |
| 9.5 | 265 " " | ..... | ..... |
| 9 | 283 " " | ..... | ..... |
| 8.5 | 300 " " | ..... | ..... |
| 8 | 321 " " | ..... | ..... |
| 7.5 | 344 " " | ..... | ..... |
| 7 | 371 " " | 148 cc. gas | ..... |
| 6.5 | 402 " " | 161 " " | ..... |
| 6 | 438 " " | 175 " " | ..... |
| 5.5 | ..... | 192 " " | ..... |
| 5 | ..... | 212 " " | ..... |
| 4.5 | ..... | 237 " " | ..... |
| 4 | ..... | 268 " " | ..... |
| 3.5 | ..... | 308 " " | 154 cc. gas |
| 3 | ..... | 361 " " | 181 " " |
| 2.5 | ..... | 436 " " | 218 " " |
| 2 | ..... | ..... | 274 " " |
| 1.5 | ..... | ..... | 367 " " |
| 1.4 | ..... | ..... | 393 " " |
| 1.3 | ..... | ..... | 424 " " |
| 1.25 | ..... | ..... | 442 " " |

**Sulphur Dioxide in Exit Gases.** Sulphur dioxide is seldom above 1% in exit gases leaving the absorption tower of the sulphuric acid plant. Generally the loss is below 0.2% on a carefully regulated

unit. The Reich method is sufficiently accurate for this determination, for all practical pruposes. If 10 cc. of N/10 iodine are used the percent $SO_2$ may be calculated by the formula:

$$\frac{11.17}{V_0 + 11.17} = \% \, SO_2.$$

$V_0$ = volume of the gas reduced to standard conditions 0° C and 760 mm.

11.17 = cc. of $SO_2$ gas equivalent to 10 cc. of N/10 iodine.

The following table is calculated on the assumption that the gas is under a pressure of 760 mm. + vapor pressure of 17 mm., at room temperature of 20° C.

| Measured Vol. | Per cent $SO_2$ | Measured Vol. | Per cent $SO_2$ |
|---|---|---|---|
| 1000 cc. | 1.22 | 3200 cc. | .38 |
| 1100 cc. | 1.09 | 3400 cc. | .36 |
| 1200 cc. | 1.01 | 3600 cc. | .34 |
| 1300 cc. | .93 | 3800 cc. | .32 |
| 1400 cc. | .87 | 4000 cc. | .31 |
| 1500 cc. | .81 | 4200 cc. | .29 |
| 1600 cc. | .76 | 4400 cc. | .28 |
| 1700 cc. | .72 | 4600 cc. | .27 |
| 1800 cc. | .67 | 4800 cc. | .26 |
| 1900 cc. | .64 | 5000 cc. | .25 |
| 2000 cc. | .61 | 5500 cc. | .22 |
| 2100 cc. | .58 | 6000 cc. | .20 |
| 2200 cc. | .55 | 6500 cc. | .18 |
| 2300 cc. | .53 | 7000 cc. | .17 |
| 2400 cc. | .51 | 7500 cc. | .16 |
| 2500 cc. | .49 | 8000 cc. | .15 |
| 2600 cc. | .47 | 8500 cc. | .14 |
| 2700 cc. | .45 | 9000 cc. | .14 |
| 2800 cc. | .44 | 9500 cc. | .13 |
| 2900 cc. | .42 | 10000 cc. | .12 |
| 3000 cc. | .41 | | |

### Sulphur Dioxide in the Inlet Gases of the Sulphuric Acid Contact System [1]

**Apparatus.** *Burette.* — This should be of the bulb type with a graduated capacity of 100 cc. the bulb holds about 87 cc.; the stem is graduated in tenths of a cubic centimeter from 0 to 12 cc. The diameter of this graduated portion is such that each cubic centimeter occupies approximately 18 mm. in length. The total length of the burette is 45 to 50 cc.

There is a constriction at the lower end of the burette, or the rubber tube connecting the burette with the levelling tube may be pinched down so that it requires 10 to 15 seconds to pass 100 cc. of mercury in or out of the burette.

[1] Method by W. W. Scott

The burette has a water jacket of sufficient capacity to include the chamber of the burette and its graduated portion. The diameter should be sufficient to accommodate the bulbed portion of the burette and a thermometer suspended by its side. Distilled water boiled free of air is used in this water jacket.

A thermometer registering from 5 to 35° graduated in tenths of a degree is left suspended in the water jacket next to the bulb.

*Leveling Tube.* — This is preferably a straight glass cylinder constricted at lower end to accommodate the heavy-walled rubber tubing connecting the tube with the burette. This tube is about 52 cm. long and has a diameter of 18 to 25 mm. The lower portion of the tube, where this is held by the hand, has a covering either of rubber, or of a heat-insulating material, to prevent warming of the mercury while making the test.

*Capillary Tube.* — The tube connecting the burette with the pipettes and the sampling pipe should have a fine capillary — the entire internal capacity should not exceed 1 cc. Details of construction show in the figure.

*Pipette.* — The cylinder of the pipette has a capacity of 150 to 175 cc. The pipette reservoir of 500 to 550 cc. capacity is recommended.

**Reagents.** *Mercury.* — Mercury is used in the measuring burette. This should be kept bright and clean and "drag no tail." To keep the gas saturated with moisture the burette should contain about 0.2 cc. of distilled water over the mercury.

*Water Solution of Chromic Acid.* — A 50% solution is recommended, although a weaker solution may be used. The strength of the reagent, however, should be over 25% of $CrO_3$.

*Sampling.* — The iron pipes carrying the gas to and from the testing apparatus have a diameter of $\frac{1}{2}$ in. to $\frac{3}{4}$ in. The line is run from the positive pressure flue near the blower to the testing apparatus and back to the minus pressure flue entering the blower, and the gas allowed to flow continuously through this shunt line.

*Making the Test.* — A volume of 100 cc. of the gas is drawn into the chamber burette (Fig. 113), by opening the stopcock *A* (*B* being closed) and lowering the leveling-tube. Stopcock *A* is closed, *B* opened and the gas expelled into the air by raising the leveling tube *H*, using care to prevent mercury bumping at the top of the reservoir. (Mercury carried into the chromic acid will reduce this reagent.) A second 100 cc. of the gas is taken and expelled as before. Finally a third 100 cc., carefully measured, is taken for the test. The top of the mercury columns in the burette and leveling tubes should be exactly level. The water surface should be at the 0 mark on the burette. Stopcock *B* is always closed during the drawing in of the gas. The temperature of the water jacket is now observed. Stopcock *A* is closed and stopcock *C* leading to the absorption pipette opened. The leveling tube is raised as before and the gas completely

passed into the pipette. The gas is drawn back into the measuring burette by lowering the leveling tube and measured. The mercury columns should stand at the same level, the reading being taken at the surface of the water over the mercury. A second pass into the pipette is now made and, if no further contraction of the gas occurs, the reading taken. The temperature is observed and a correction made of 0.36 cc. per degree (centigrade) rise or fall of temperature. This correction is added if the temperature rises, or is subtracted if the temperature falls.

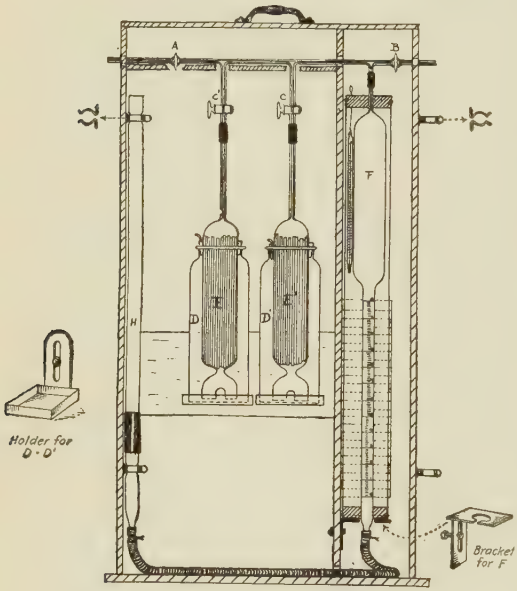



Fig. 113. Scott's Gas Analysis Apparatus.

The contraction of the gas, due to absorption of $SO_2$, in terms of cc. gives the direct per cent reading.

**Example:**

100 cc. of gas taken.
Final reading 91.5, i.e., direct = 8.5 cc.
Temperature change = 0.4° rise.
Then $8.5 + (.4 \times .36) = 8.6\%$ $SO_2$.

Tests should be made in duplicate, each Orsat having two pipettes. Very little more time is required to run the check test if the following method is observed. The first sample is taken and passed into one of the pipettes; a second sample, immediately taken, is passed into the second pipette. The first sample is now again measured and then returned to the first pipette and then the check sample measured and returned to its pipette. The first sample is again measured and if a further contraction is observed it is again passed into its pipette and the process repeated with the second sample. By thus alternating the tests and allowing the gas to stand in the pipettes the second pass will cause complete absorption of $SO_3$, third pass seldom being necessary.

## TANTALUM AND COLUMBIUM

**Ta, at.wt. 181.5; sp.gr. 14.49; m.p. 2900°; oxides $TaO_2$, $Ta_2O_5$; Cb, at.wt. 93.5; sp.gr. 7.06; m.p. 1950°; oxides CbO, $CbO_2$, $Cb_2O_5$**

Tantalum and columbium occur commonly with tungsten in nature. In the following minerals, however, tantalum and columbium form the more important constituents:

*Columbite*, $(Ta\ Cb)_2(Fe\ Mn)O_6$;[1] *pyrochlore*, $RCb_2O_6R(Ti.Th)_3$; *hatchettolite*, $2R(CbTa)_2O_6$ or $R_2(Cb.Ta)_2O_7$; *fergusonite*, $R(Cb.Ta)O_4$; *yttrotantalite*, $RR(Cb.Ta)_4O_{15}.4H_2O$; *samarskite*, $R_3R_2(Cb.Ta)_6O_{21}$.

Tantalum is used in electric light filaments; it is also used for hardening steel for drills, files, cutting edges, watch springs, and pen points. It is used in rectifiers for alternating currents.

### DETECTION

The finely powdered mineral is digested with strong hydrochloric acid, followed by concentrated nitric acid and the mixture taken to dryness. The residue is treated with hydrochloric acid, diluted with water, boiled and filtered. The residue is digested with warm ammonium hydroxide to remove tungsten and the solution filtered from the insoluble material, in which tantalum and columbium will be found, if present in the sample.

Decomposition of the material may be effected according to the procedure described for the detection of tungsten.

The residue obtained is digested, in a platinum crucible, with hydrofluoric acid and a saturated solution of potassium fluoride added. The mixture is evaporated to small volume and allowed to cool slowly. Tantalum will separate in acicular rhombic crystals (solubility — 1 part of the salt in 200 parts of water) as potassium fluotantalate $2KF.TaF_5$; columbium separates in plates as the double fluoride, $2KF.CbF_5$, if HF is in excess, or as a double oxy-fluoride $2KF.CbOF_5$, if HF is not in excess; the columbium salt being much more soluble (1 part of the salt in 12 parts of water) crystallizes after the crystals of tantalum have formed.

The crystals may be examined under a lens and then treated as follows: The needle-like crystals are heated in a shallow platinum dish or crucible cover with strong sulphuric acid to fumes, the cooled mixture is transferred to a test-tube with water and boiled to precipitate the tantalic acid. An opalescent solution is obtained when

[1] Columbite-Tantalite (Fe, Mn) $(Cb,Ta)_2O_6$, black often bright, opaque, brittle mineral. In large masses and in pebbles in tin gravels; streak dark red to black; hardness 6.

this precipitate is treated with an excess of hydrochloric acid. Metallic zinc added to this solution produces no color. A light-brown precipitate is obtained with tannic acid in the presence of tantalum. If the crystals of columbium salt are treated in the same way, metallic zinc added to the acid solution will give a blue coloration, and tannic acid an orange-red coloration. Tantalic acid fused with sodium metaphosphate gives a colorless bead (distinction from silica). The bead moistened with $FeSO_4$ and heated in the inner flame is not colored red. Columbic acid fused in the same way gives a blue bead in the reducing flame, and a red bead by addition of $FeSO_4$ and heating in the flame.

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

The statements made for solution of the sample in determinations of tungsten apply here also. It is well to keep the following facts in mind: Tantalum is insoluble in the common mineral acids — hydrochloric, nitric and sulphuric acids, but dissolves in hydrofluoric acid. Columbium is insoluble in hydrochloric, nitric and in nitro-hydrochloric acid, but dissolves in hot concentrated sulphuric acid. The oxides $Ta_2O_5$ and $Cb_2O_5$ fused with KOH form soluble salts. $Cb_2O_5$ (not strongly ignited) is soluble in acids, from which $(NH_4)_2S$ and $NH_4OH$ precipitate columbic acid (containing ammonia). Freshly precipitated tantalic acid is soluble in acids, and reprecipitated by $NH_4OH$. The acid dissolves readily in HF.

**Tantaliferous Minerals.** — Although decomposition may be effected by fusion with potassium acid sulphate, fusion with potassium hydroxide is recommended as being the best flux for opening the minerals. Simpson's process is as follows:[1]

Three grams of pure potassium hydroxide are fused in a nickel or silver crucible and the finely powdered mineral (0.5 gram) added, the contents mixed by gently rotating the crucible and fusion kept at a dull red heat for ten minutes longer. The crucible placed in a hole in an asbestos board, Fig. 110, is heated over a free flame for half an hour, the sample being covered. The lid is removed and allowed to cool reversed, if any material clings to this. The cooled crucible, placed in a beaker, is two-thirds filled with distilled water, and a clock-glass immediately placed over the beaker. After the violent reaction has subsided the contents of the crucible are poured into about 10 cc. of dilute hydrochloric acid (sp.gr. 1.08) in a 300 cc. beaker, and the crucible, basin and the lid washed with water, followed by about 20 cc. of the dilute acid, and again with water, adding the washings to the remaining solution. The total volume of the solution should occupy from 80 to 100 cc. A drop or two of alcohol are added to destroy any potassium manganate formed.

**Isolation of Columbium and Tantalum Oxides.** — Separation from iron, manganese, copper, cobalt, nickel, calcium, magnesium, titanium, and tin. The solution obtained above is boiled with 5 to 10 cc. of hydrochloric acid (sp.gr. 1.16) (less acid may be used if titanium is absent). Columbium and tantalum hydroxides are precipitated. The solution is now diluted to 200 cc. and boiled for fifteen minutes longer to make sure that the precipitation is complete. After settling, the clear solution is decanted through a close-grained filter and the residue, having been transferred to the filter, is washed with dilute hydrochloric acid (sp.gr. 1.08) until the washings give no indication

[1] E. S. Simpson, Chem. News, 99, 243, 1909.

of iron. The residue may contain tantalum, columbium, tungsten, silica, antimony, and tin. The greater part of the tin, titanium, and all of the iron, manganese, cobalt, nickel, copper, calcium, and magnesium are removed in the filtrate.

NOTES. If the filtrate becomes turbid, it is advisable to dilute the solution and repeat the boiling to recover the columbium and tantalum that may still be in solution.

In the presence of appreciable amounts of titanium a soluble double chloride of columbium and titanium is formed, so that the precipitation of columbium is not complete. (See L. Weiss and Landecker, Chem. News, 101, 2, 13, 26, 1910.) The formation of this compound is hindered by the addition of an oxidizing agent — sodium nitrate — to the alkali.

**Removal of Tin, Antimony, Tungsten and Silica.** — *Tungsten* is removed by digesting the moist precipitate with ammonium hydroxide or sulphide, tungsten being soluble in these reagents. Antimony and tin are also removed.

*Silica* is volatilized by heating the residue with sulphuric and hydrofluoric acids according to the standard procedure.

*Tin.* — The oxide may be reduced with hydrogen passed over the heated residue within a boat placed in a combustion tube. The tin may now be dissolved out with hydrochloric acid.

### Determination of Columbium and Tantalum

The insoluble residue obtained, freed from other elements by the procedures outlined, is ignited at a red heat for fifteen or twenty minutes and the residue weighed as $Cb_2O_5 + Ta_2O_5$.

### Separation of Columbium and Tantalum, Selenium Oxychloride Method.[1]

The method depends on the solubility of columbium oxide and the comparative insolubility of tantalum oxide in a mixture of sulphuric acid and selenium oxychloride as found by Victor Lenher.[2]

The method worked out by H. B. Merrill is as follows:

The oxides are separated together with titanium dioxide from the other elements by the usual methods and the total percentage of titanium and columbium pentoxides (with titanium) is determined.

A weighed sample (0.2–0.3 g.) of the ignited oxides is boiled with 50 cc. of a 1 : 1 mixture of selenium oxychloride and strong sulphuric acid (sp.gr. 1.84) in an Erlenmeyer flask, on a sand bath for half an hour, avoiding heating to voluminous fumes. After cooling the solution is carefully decanted from the residue, with suction, through asbestos in a Gooch crucible that has been weighed. The filtrate is

[1] Henry Baldwin Merrill, Jour. Am. Chem. Soc. **43**, 2378, (Nov. 1921).
[2] Victor Lenher, Jour. Am. Chem. Soc. **43**, 21, (1921).

poured into a large volume of water and the solution boiled. A white precipitate indicates the presence of columbium. The residue in the flask is again extracted with 20 cc. of the reagent for fifteen minutes, the extract being poured through the asbestos filter and the filtrate tested as before for columbium. The process is repeated until the filtrate upon hydrolysis gives only a faint precipitate, due to traces of dissolved tantalum pentoxide. Three or four extractions are usually sufficient.

The undissolved tantalum pentoxide is transferred to the crucible with a jet of water from a wash bottle. Washing unnecessary. The crucible is ignited and weighed, the gain in weight representing tantalum pentoxide.

Columbium (with titanium) is determined by difference. If titanium is present it is determined colorimetrically in a separate sample and its amount deducted from columbium.

## THORIUM

**Th, at.wt. 232.4; sp.gr. 7.7; 11.00; m.p. 1700°; oxides $ThO_2$**

The estimation of thorium is required chiefly in the fabrication of incandescent gas mantles. Raw materials such as *monazite* (C,La,Di,Th) $PO_4$ and *thorite* ($ThSiO_4$) [1] are generally used. The former usually contains from 2 to 4% of thorium while the latter runs as high as 81.5%. Thorium nitrate in a rather impure state is the chief intermediate product. The finished mantles generally contain 99% $ThO_2$ and 1% $CeO_2$.

### DETECTION

(1) By means of the spectroscope. Thorium shows lines of greatest intensity in the arc spectrum at 4863.3 and 4919.9. In the spark spectrum lines of greatest intensity at 3221.4, 3300.6, 4382.1. 4391.1.

(2) By the addition of $H_2O_2$ to a neutral solution of the nitrate containing ammonium nitrate. See page 567.

(3) By radio activity. Thorium compounds possess the power of continually emitting Becquerel rays and radio active emanations.

### Preparation and Solution of the Sample

**"A" Silicates (as thorite, etc.)** are decomposed by treatment with ten times their weight of fuming hydrochloric acid. This treatment usually suffices, but in cases where an insoluble residue still remains it is fused with ten times its weight of sodium carbonate in a large platinum crucible. The fusion is dissolved in hydrochloric acid and added to the solution obtained from the first extraction. After the silica and the metals of the first group are removed in the usual way the solution is freed from $H_2S$ by boiling. The thorium together with the other rare earths, calcium, magnesium, etc., are then present as chlorides and the necessary separations made as detailed under gravimetric determination.

**"B" Phosphates (as Monazite, etc.)** — (1) *By Fusion with Potassium Acid Sulphate.* — 0.5 gram of the finely pulverized material is mixed with 10 grams of potassium acid sulphate in a large platinum crucible, covered and heated until gentle fusion takes place and no

[1] Orange yellow or black tetragonal crystals; translucent to transparent; resinous lustre; streak orange to brown; hardness 4.5–5.

further gas is given off. Then ignite over free flame for a few minutes, cool and treat with a little water and hydrochloric acid, until complete decomposition takes place. Boil for a few minutes, allow to cool and settle and decant off the clear liquid. The residue is treated with concentrated hydrochloric acid. Dilute and filter from the residue of silicic and tantalic acids. The filtrate then contains the thorium, etc., as chlorides. Determinations are made as detailed under gravimetric methods following.

(2) *By Sulphuric Acid Extraction.* — The finely pulverized sample is mixed with sufficient $H_2SO_4$ to form a paste and the mass heated gently at first, then gradually with increasing heat to low redness. After cooling, the rare earths are dissolved from the mass with cold water. The thorium is then present in the solution as sulphate. After removal of the base metals in the usual way determinations are carried out as detailed below.

**"C" Oxides (as gas mantles, etc.).** — In the case of gas mantles the organic matter is first burned off and the resulting oxides heated with three times their weight of strong $H_2SO_4$ in a porcelain casserole. The mixture is heated on the sand bath at a temperature slightly below that required to drive off fumes of $SO_3$ for a few minutes. After cooling, the contents are diluted with a small quantity of water and allowed to stand for several hours. The sulphates completely dissolve and the sample is ready for the gravimetric estimation as detailed.

The following properties of thorium are of value in its isolation:

(1) The hydroxide is insoluble in an excess of the precipitant.

(2) The sulphate forms double salts with $K_2SO_4$, which are insoluble in an excess of the reagent.

(3) Thorium oxalate readily forms a double oxalate with ammonium oxalate in an excess of the reagent.

(4) Thorium is precipitated together with the rare earths by oxalic acid.

(5) Thorium and cerium may be separated from all of the other earthy metals if the hydroxides recently precipitated are suspended in water containing four to five times their weight of caustic soda and a current of chlorine gas passed through the solution. All of the other metals dissolve. The insoluble residue left under these conditions is gelatinous like aluminum hydroxide.

(6) Thorium may be completely separated from cerium by precipitation with $H_2O_2$ from a neutral solution containing 10% of ammonium nitrate, the thorium being precipitated as the peroxide, which on ignition readily changes to the oxide, $ThO_2$. See chapter on Cerium.

(7) Thorium may be precipitated by sebacic acid. See method given in chapter on Cerium.

(8) Thorium is quantitatively precipitated at room temperature as $Th(MoO_4)_2$ from a 7% acetic acid solution containing one gram of sodium acetate, by means of a solution of ammonium molybdate added from a burette. The other rare earths formed in monazite sand are not precipitated under these conditions. Dephenyl carbazide is used as an external indicator, a drop showing a rose color when an excess of molybdate has been added. The color is apt to fade. Thorium may be determined volumetrically by this means.[1]

[1] F. J. Metzger and F. W. Zons, J. Ind. Eng. Chem. 4, 1912, p. 495.

## GRAVIMETRIC METHOD FOR DETERMINING THORIUM

The solution of the ignited oxalates dissolved in HCl or $H_2SO_4$ (freed from the base metals and silica, by precipitation as oxalates and filtration), is made nearly neutral with ammonium hydroxide and the rare earths reprecipitated by the addition of oxalic acid in solution. In the case of monazite sands when 0.5 gram sample is used 1 gram of oxalic acid is generally sufficient, but in any case the precipitate should be allowed to settle and the clear solution tested by the further addition of oxalic acid. After standing at least twenty-four hours, it is filtered and washed thoroughly with water. The precipitate is then washed into a casserole and treated with strong nitric acid, a little added at a time until complete decomposition has taken place, then evaporated to dryness on the steam bath to remove the excess acid. A second evaporation with water should follow in cases where the precipitate is appreciable. Take up with 10% ammonium nitrate in sufficient quantity to cause a dilution of one part of thorium nitrate in 100 parts of water. It is heated to 60°–80° C. and the thorium precipitated with 20 cc. of pure 3% $H_2O_2$ solution for each 100 cc. solution. The precipitate, which is usually colored yellow by traces of cerium peroxide, is filtered at once and washed with hot water containing ammonium nitrate. By reprecipitating after solution in nitric acid and neutralizing the excess acid with ammonia pure thorium peroxide may be obtained. The precipitate is ignited in a platinum crucible and weighed as $ThO_2$.

Thorium nitrate is assayed by precipitating the thorium as peroxide according to the details given above.

## DETERMINATION OF MINUTE AMOUNTS OF THORIUM, JOLLY'S METHOD [1]

Solids after pulverizing are fused with an alkali carbonate at 1000° C. and the fusion extracted with water. The residue is dissolved in dilute hydrochloric acid and set aside for some days in order to allow thorium disintegration products to develop. The thorium is then determined by boiling off the emanations in a constant stream of air which is passed through an electroscope. The rate of discharge of the electroscope is compared with that produced when a known amount of thorianite was tested. It is necessary to boil the solutions before testing to expel any radium emanation that may be present.

[1] J. S. C. I., 8, Vol. 34, 422.

## DETERMINATION OF THORIUM IN MONAZITE SAND

The following method of Carney and Campbell [1] is recommended by J. P. Bonardi. The rare earths, iron, titanium and zirconium do not interfere.

**Preparation and Solution of the Sample.** — Fifty grams of the dry sand are weighed and transferred to a porcelain dish (500 cc., 7 in. deep), 100 cc. of strong sulphuric acid are added, stirring into the sand. The dish is placed in a sand bath and heated over a flame at such temperature as to cause but slight fumes from the sulphuric acid. The material is stirred every half hour. In one to two hours the mass swells and turns white. Five hours are generally sufficient to disintegrate the sand, but it is desirable to digest for twelve hours longer. The mass is then allowed to cool.

An 800 cc. beaker is filled three-fourths full with finely crushed ice. By means of a porcelain spatula the digested material is transferred in small portions to the beaker, stirring well after each addition. When practically all the sample has been removed from the dish, that remaining is mixed with a little crushed ice and transferred to the beaker. The whole is allowed to rise to room temperature. Except for the residue of sand, which consists mainly of silica and ilmonite, the contents of the beaker are completely transferred to a liter volumetric flask, and the solution diluted to 1000 cc.

NOTE. — The solution may be cloudy from some silica in suspension. This is later removed as soluble sodium silicate by a later sodium hydroxide treatment.

**Analysis of the Solution.** — Fifty cc. of the solution are transferred to an 800 cc. beaker and made up to a volume of 450 cc. with distilled water. The acidity of the solution will be about .2 to .35 N. The beaker is covered with a watch glass, a stirring rod placed in it, and the solution heated to boiling, stirring occasionally to prevent bumping. 5 cc. of sulphurous acid are added to reduce the iron and cerium. If the solution remains yellow, 3 to 4 drops of sodium thiosulphate solution (10%) will complete the reduction. 15 cc. of sodium pyrophosphate solution (50 grams per liter) are added by means of a pipette. The solution is boiled for five minutes then immediately filtered. The filtrate is discarded.

NOTE. — Clouding of the filtrate is due to oxidation of iron and cerium and precipitation of these by the excess of pyrophosphate.

With the aid of a policeman and acidulated water (1 drop HCl per 200 cc. of water) the last traces of thorium pyrophosphate are transferred to the filter paper. 120 cc. of sodium hydroxide solution (25%) are poured into the beaker and this set aside for subsequent use.

[1] R. J. Carney and E. D. Campbell, Jour. Am. Chem. Soc., 36 (1914), pp. 1134–1143.

After being drained, the filter paper and precipitate are lifted out of the funnel and placed on a piece of clean blotting paper, and dried thus for 2–3 minutes. The filter paper is doubled over the precipitate and rolled into a cylinder (removing from the blotting paper) and the material dropped into a 300 cc. Kjeldahl flask. About 20 cc. of strong sulphuric acid are added and the flask gently shaken to char the filter. By means of a long stem funnel 2 to 3 cc. of fuming nitric acid are added to the mass in the flask (Hood). (In case of excessive foaming cool in water, under the tap.)

When foaming has ceased the mixture is heated over a low flame gradually increasing the heat until sulphuric fumes are freely evolved from the mouth of the flask. The heating is continued until the contents of the flask become practically colorless (or a faint straw color). It may be necessary to add more nitric acid (cooling the contents of the flask before addition) and again heat.

After the mass has cooled, the funnel is rinsed into the flask, and water added to make up a volume of about 100 cc.

When the material has gone into solution (cloudiness will be due to silica) it is poured into the sodium hydroxide in the beaker reserved for this purpose. The flask is rinsed out three or four times and the rinsings added to the NaOH solution. The volume is made up to 450 cc. and the liquid boiled for about 5 minutes, then filtered hot, and the beaker rinsed once with hot water into the precipitate.

The precipitate is allowed to drain and then placed with the filter back into the beaker. 12 cc. of hydrochloric acid (1.19) are poured over the precipitate and allowed to stand for 5 minutes with occasional shaking. All of the hydroxide should dissolve. 100 cc. of hot water are added and the filter stirred, then drawn up on the side of the beaker and allowed to drain. The filter (held by a glass rod) is rinsed into the beaker with hot water, then rolled and squeezed by means of the fingers to remove the adhering water. The wad is placed in the Kjeldahl flask.

The volume of the solution is made up to 450 cc. and thorium again precipitated as pyrophosphate, and the treatment described above repeated, the thorium being converted into sulphate, hydroxide and chloride by the successive steps. Only 10 cc. of hydrochloric acid are used in making the second chloride solution. The final solution diluted to 100 cc. is filtered into an 800 cc. beaker. The first beaker is washed out several times with hot water adding this to the second until the volume is 450 cc. Traces of iron and rare earths are now removed.

The solution is heated to boiling and 35 cc. of oxalic acid solution (60 grams per liter) are added drop by drop from a burette and then boiled for 15 minutes. Thorium is precipitated free from titanium and zirconium. The beaker is placed on the steam bath and allowed to remain, covered, at least 5 hours or preferably overnight.

The precipitate is filtered on a 9 cm. filter, the beaker copped out, using acidulated water (1 drop of HCl per 200 cc. $H_2O$) and pouring over the precipitate. After draining, the precipitate is placed in a weighed platinum crucible over a low flame and dried, the heat then raised and the ignition continued with strong heat for about 30 minutes. The residue should be snow-white.

The crucible is cooled in a desiccator and the residue weighed as $ThO_2$.

$$ThO_2 \times 0.879 = Th$$

A greater part of this chapter was compiled by R. Stuart Owens, Consulting Chemist, New York City.

## TIN

**Sn, at.wt. 118.7; sp.gr. 6.56; m.p. 232°; b.p. 2275°; oxides $SnO_2$ and SnO**

The estimation of tin is required in connection with the analysis of tin ores, dross, ashes, dust, tin plate, alloys such as solder, canned foods, and general analysis.

### OCCURRENCE

Tin is seldom found in native state, it occurs to a slight extent as the sulphide $SnS_2$, but is widely distributed as cassiterite or tin stone, $SnO_2$.

**Minerals.** — *Stannite,* Tin Pyrites, ($Cu_2S.FeS.SnS_2$), a massive, brittle, opaque, granular mineral, with metallic lustre, steel gray to nearly black; black streak; hardness 4.

*Cassiterite.* — Stream Tin, Tin Stone, a brown to nearly black (sometimes gray, red or yellow), opaque to translucent, hard, brittle and heavy mineral with adamantine to dull lustre; white or pale brown streak; hardness 6–7. Often in kidney shaped masses or rounded pebbles, or with radiated structure.

The mineral placed on a piece of zinc in dilute hydrochloric acid becomes coated with gray metallic tin.

*Varieties.* — Tin Stone, Wood Tin, Stream Tin.

### DETECTION

Tin is separated, together with arsenic, antimony, gold and platinum, from the hydrogen sulphide precipitate of the metals of the second group, by the action of yellow ammonium sulphide. (Normal ammonium sulphide does not readily dissolve the sulphides of tin.) If the ammonium sulphide solution is acidulated with hydrochloric acid and the acid solution reduced with iron, antimony, arsenic, platinum and gold are precipitated in the metallic form. The presence of tin, which is present as stannous chloride, is indicated by the reducing action of the solution on mercuric chloride, a white precipitate of HgCl or a gray precipitate of Hg being thrown down.

Reduce the hydrochloric acid solution of the sample by means of a small piece of iron wire. Treat with an excess of cold potassium hydroxide. Filter if the solution is not clear. Add an ammoniacal solution of silver nitrate. (One part of $AgNO_3$: 6 parts of $NH_4OH$.) A brown precipitate of metallic silver indicates the presence of tin. Antimony, arsenic, platinum and gold are precipitated by the iron,

while all of the heavy metals remaining, except lead, tin, aluminum, chromium, and zinc, are removed by the treatment with potassium hydrate.

Welch and Weber recommend the following method for detection of tin: Add 10 cc. concentrated hydrochloric acid to the superficially-dried precipitated sulphides from the ammonium sulphide separation. Filter off arsenic which does not decompose. Dilute filtrate to 70 cc. volume. Saturate with $H_2S$. Heat to expel excess $H_2S$. Add 5 cc. of hydrogen peroxide and heat until the precipitate is redissolved. Add 5 to 10 grams of oxalic acid and pass $H_2S$ into the hot solution. Antimony separates as a red sulphide. Filter. The filtrate contains the tin. Reduce with test lead and add mercuric chloride. A white or grayish precipitate indicates the presence of tin.

## GRAVIMETRIC METHODS

### Preparation and Solution of the Sample

As the oxides of tin are not readily soluble in acids the tin can be most easily removed by assay. Ores, slags, dross, and ashes are first subjected to the assay process. The button obtained is then analyzed either volumetrically or gravimetrically by one of the methods given below. Having the weight of the button and the per cent of tin in it, the per cent of tin can be calculated.

### Assay of Tin by the Cyanide Process

The theory of this method is that the oxides are reduced to the metal by the action of potassium cyanide, the reaction being represented as follows:

$$SnO_2 + 2KCN = Sn + 2KCNO.$$

Potassium cyanide reduces other metals also so that the button obtained is not pure.

**Procedure.** — Take 100 grams of the sample which has been dried and finely powdered. (For complete analysis the moisture should be determined in the usual way.) Mix thoroughly with four times its weight of powdered potassium cyanide. Place about 1 in. of potassium cyanide in the bottom of a number H (height $5\frac{7}{8}$ ins., diameter $3\frac{3}{4}$ ins.) Battersea clay crucible. Place the mixture of sample and cyanide on top of the cyanide in the crucible and cover with enough more cyanide to fill the crucible to within 1 in. of the top.

Place the crucible in the assay furnace and heat slowly until it has been thoroughly warmed and the cyanide begins to melt. Then increase the heat gradually to a pure white, taking care that the cyanide does not boil over. Grasp the crucible with the tongs and tap it gently on the hearth to assist in settling the metal. Continue the heating until all of the organic matter has disappeared, adding more cyanide from time to time if necessary. Near the end of the process the molten mass becomes clear and transparent and finally pasty and translucent. When this last condition appears, remove the crucible from the furnace and allow it to cool slowly at the temperature of the room.

When cool, break the crucible and slag away from the button. The appearance of the button and the slag immediately surrounding it indicates whether or not the process has been properly manipulated. The button itself should be firm and compact and the slag around it should be white or greenish in color. If the button is spongy or if the slag has a dirty black color, the assay should be discarded and a new determination made, using a fresh sample.

Weight of Button = per cent of Metal in Sample.

NOTE. This process should be carried on under a hood in a segregated room, and every precaution should be taken to avoid breathing the fumes.

### The Sodium Carbonate Method

The sample is fused with equal parts of sodium carbonate and sulphur. The fusion is then dissolved in water. The tin goes into solution as a thiostannate of sodium. Iron and copper are then separated by the addition of sodium sulphite, leaving arsenic, antimony and tin in solution.

**Fusion with Sodium Hydrate.** — The sample of ore is fused with ten times its weight of sodium hydrate. The process is carried out in an iron crucible and then transferred to nickel. The fused mass is dissolved in water and the tin determined in the usual way.

**Reduction by Means of Hydrogen.** — The ore may be reduced by strongly igniting in a porcelain tube in a current of hydrogen. The reduced metal is then dissolved in hydrochloric acid and the tin estimated by a standard method.

**Fusion with Sodium Peroxide.** — J. Darroch and C. Meiklejohn opened ores, slags, etc., by fusing with sodium peroxide in a nickel crucible. They dissolve the fused mass in hot water and acidify with hydrochloric acid. The sample is then ready for the necessary separations.

### Notes on Separations

Tin is separated from iron, aluminum, chromium, etc., by the insolubility of its sulphide in dilute hydrochloric acid. Tin, together with antimony, arsenic, platinum and gold, is separated from lead, mercury, copper, cadmium and bismuth, by the solubility of its sulphide in yellow ammonium sulphide. Antimony, arsenic, platinum and gold are precipitated as metals from a hydrochloric acid solution by the action of metallic iron, leaving tin in solution.

A few special separations are of interest.

**Tin and Lead.** — For the analysis of an alloy of lead and tin, it is usually preferable to make the estimations on different samples. In this case, lead is estimated by Thompson's method and the tin by Baker's modification of the iodine method. Lead can also be separated from tin by the method given below for the separation of tin and copper.

**Tin and Copper.** — This alloy can be dissolved in concentrated hydrochloric acid by the addition of potassium chlorate. A large excess of ammonium tartrate is added and the solution made alkaline with ammonia. Copper is then precipitated as sulphide by the addition of hydrogen sulphide water until no more precipitate is formed.

**Tin and Antimony.** — Antimony is separated, in the metallic form, from the hydrochloric acid solution of the alloy, by the action of metallic iron placed in the solution. The tin may be determined by the iodine method without the removal of the antimony. If the antimony is desired, it may be filtered off and determined in the usual way.

As in the case of lead, it is usually quicker and more accurate to make these determinations on separate samples. The tin can be determined by the iodine method. The antimony can be determined volumetrically by various methods, preferably the bromate. (See chapter on Antimony.)

**Tin and Phosphorus.** — One-half gram of the alloy is dissolved in 15 cc. of concentrated hydrochloric acid containing potassium chlorate. This is diluted to 200 cc. with water and warmed. It is then treated for a long time with hydrogen sulphide gas. The tin is all precipitated as sulphide while the phosphorus remains in solution.

**Tin and Iron and Aluminum.** — Tin is separated from iron and aluminum by precipitation, as sulphide, from the hydrochloric acid solution.

Iron may also be separated from tin with copper, and lead by precipitation as sulphide from the alkaline ammonium tartrate solution.

**Tin and Tungstic Acid.** — Donath and Mullner separate tin oxide from tungstic acid by mixing the sample with zinc dust and strongly igniting in a covered crucible for fifteen minutes, boiling with dilute hydrochloric acid, oxidizing with potassium chlorate to change the blue tungstic oxide to tungstic acid and diluting with water. It is then allowed to stand overnight and filtered. The tin is in solution.

### Gravimetric Determination of Tin in Alloys

**Solutions Required.** — *Dilute Hydrochloric Acid*: Mix 500 cc. of HCl, sp.gr. 1.20, and 500 cc. of distilled water.

*Dilute Sulphuric Acid:* Mix 300 cc. of $H_2SO_4$, sp.gr. 1.84, and 600 cc. of distilled water.

*Dilute Ammonia:* Mix 100 cc. of $NH_4OH$, sp.gr. 0.90 and 900 cc. of distilled water.

*Ammonium Acetate Solution for Washing:* Dissolve 10 g. of ammonium acetate in 300 cc. of distilled water. Make slightly acid with acetic acid and saturate with $H_2S$ gas.

**Method.** — In a 150 cc. beaker dissolve 2 g. of bronze in a mixture of 10 cc. of HCl, sp.gr. 1.20, and 5 cc. of $HNO_3$, sp.gr. 1.42. Dilute to about 75 cc. with distilled water. Add $NH_4OH$, sp.gr. 0.90, until the basic salts of copper have dissolved and the solution has become a deep blue. Boil and allow to settle, and filter on a closely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with hot dilute HCl. Dilute the solution to about 100 cc. Add $NH_4OH$, sp.gr. 0.90, until a permanent precipitate forms. Heat the solution to boiling, allow to settle, filter and wash as before. Dissolve the precipitate on the filter with boiling hot dilute $H_2SO_4$, washing the paper very thoroughly with this acid. Add $NH_4OH$, sp.gr. 0.90, cautiously until the precipitate which forms at first dissolves rather slowly. Allow the solution to stand for some hours and if any lead sulphate forms filter it off. Dilute the solution to about 200 cc. and saturate it with $H_2S$ gas. Filter the precipitated tin sulphide off on double papers and wash with ammonium acetate solution, retaining the filtrate and washings from the iron determination. Dry the precipitate and place it with the papers in a porcelain crucible which projects part way through a hole in a piece of asbestos board. Heat slowly until any free sulphur has been driven off, but without allowing the sulphur to burn. When the sulphur has been expelled, place the crucible on a triangle and ignite slowly at first and finally at the full heat of the burner. If the precipitate weighs more than 20 mg. heat to constant weight, using a blast lamp. Weigh as $SnO_2$, which contains 78.81 per cent of tin.

*Accuracy:* Duplicate determinations should check within 0.06 per cent of tin.

Notes. If, during ignition, the sulphur is allowed to burn, some tin sulphate may be formed, causing high results. On the other hand, low results may be caused by too high heat, which causes spattering and volatilizes some tin sulphide.

Tin and iron are best determined on the same sample, retaining the filtrate from the tin sulphide precipitate to use for the iron determination.

## VOLUMETRIC DETERMINATION OF TIN

Volumetric methods for the determination of tin are based upon the reducing power of stannous compounds. They vary according to the oxidizing agent used and the details of manipulation.

### LENSSEN'S IODINE METHOD AS MODIFIED BY BAKER [1]

This method is a modification of Lenssen's Iodine Method for the determination of tin in alkaline solutions. It is especially applicable to the determination of "salts of tin" in canned foods and to the estimation of tin coating on tin plate, but is accurate, rapid and very satisfactory for alloys and general analysis.

The method is based on the action of iodine in the presence of stannous chloride in hydrochloric acid solution. The reaction involved is:

$$SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI.$$

Iron, lead and antimony do not interfere with the reaction. Copper in small quantities does not interfere with the determination, but if it is present in large quantities as a salt, it is likely to produce low results. Determinations made by the writer show that results are accurate when less than 10% of copper, as copper chloride, is present. Larger amounts gave consistently low results. The reason for this fact centers around the difficulty of reducing all the copper to the cuprous form. If any $CuCl_2$ is left in the solution, it reacts with the potassium iodide of the iodine solution, causing the precipitation of CuI and the liberation of free iodine.

$$2\ CuCl_2 + 4KI = Cu_2I_2 + 4KCl + I_2.$$

Copper present as the metal is not easily soluble or goes into solution in the reduced form and is not likely to disturb the determination.

**Solutions — Standard Tin Solution.** — Dissolve 5.79 grams of Kahlbaum's C.P. tin in C.P. hydrochloric acid.[1] The solution of the tin is effected by placing about 150 cc. of HCl in an Erlenmeyer flask, together with the tin, and boiling. After the tin has all been dissolved, transfer to a volumetric liter flask and make up to the mark with dilute hydrochloric acid.

1 cc. = .00579 gram of Sn.

[1] The details of this method as given were developed by Mr. H. A. Baker at the laboratory of the American Can Company, and have been modified in accordance with the findings of several years of experience.

**Standard Iodine Solution.** — Dissolve 12.7 grams of C. P. iodine in a water solution of 20 grams of potassium iodide. Make up to one liter and standardize against the standard tin solution. For tin plate analysis, it is convenient to adjust the iodine solution so that 1 cc. equals exactly .00579 gram of tin. Then, if a sample of the plate having a total surface of 8 sq.ins. is taken, 1 cc. of the iodine solution is the equivalent of one-tenth of a pound per base box.[1]

**Indicator.** — Dissolve 5 grams of pure soluble starch in 1 liter of water.

**Air-free Water.** — Dissolve 12 grams of bicarbonate of soda in one liter of water. Add 20 cc. HCl and allow the resulting gas to escape. Keep in a stoppered bottle.

**Procedure.** — For practical purposes, take a sample, such that the tin content will be between .2 gram and .5 gram. A larger sample should be taken for extreme accuracy in order to decrease the possible technical error. Place the sample in flask *A* of the Sellars apparatus, Fig. 114, together with 100 cc. of conc. C. P. HCl.[2] Stopper the flask and connect tubes *B* and *D*, as shown in the illustration. Boil until the metal is all dissolved. This point is indicated by the cessation of the hydrogen evolution and the appearance of large well-developed bubbles. If a sufficient amount of metallic iron is present in the sample, complete reduction is assured. If no iron was present in the sample, or if there was not enough to reduce all of the tin, make sure that the tin is all converted to the stannous form by adding aluminum foil (about 1 gram). Replace the stopper and connect as originally. Boil until normal bubbles reappear. Open cock *C* to allow $CO_2$ gas to enter. Place the flask in cooling bath *F* without disconnecting the apparatus. After the solution has become thoroughly cool, disconnect tubes *B* and *D* from the splash bulbs. Wash the bulbs with "air-free" water, allowing the washings to drain into the bulk of the sample. Remove the stopper and wash down the sides of the flask. About 50 cc. of water should be used in the washing so that the final sample contains about 25% HCl. Add 5 cc. of starch solution and titrate with the standard iodine solution.

$$\frac{\text{cc. iodine} \times .00579 \times 100}{\text{Weight of Sample}} = \text{per cent Sn},$$

or

$$\frac{\text{cc. iodine}}{10} = \text{pounds per "base box."}$$

[1] "Basebox" — 112 sheets of tin, $14 \times 20$ ins.

[2] The addition of a drop or so of antimony chloride (10% sol.) accelerates, by electro-couple action, the decomposition of tin by HCl. The metallic antimony precipitated does not interfere with the determination.

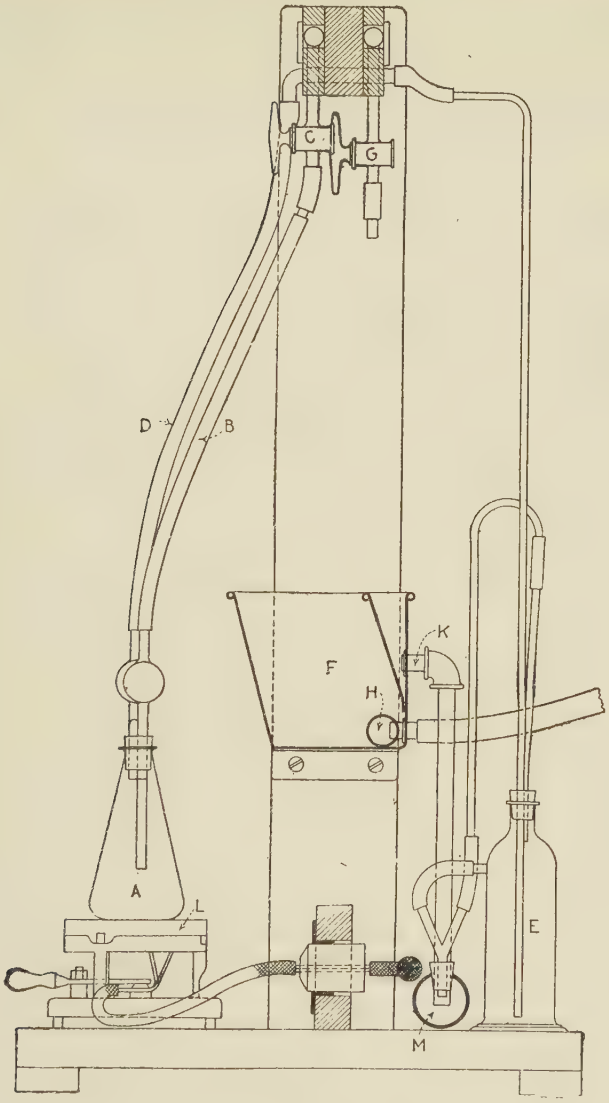



FIG. 114. Sellars' Apparatus.

**The Sellars Apparatus.** — This apparatus is a device designed by Mr. W. S. Sellars, American Can Co., for the purpose of facilitating the solution of tin samples out of contact with air. Added to this

advantage, it is equipped with a water cooler. It is also constructed so that the tubes and scrubbing bottles can be cleaned by flushing with water. The use of this apparatus practically eliminates the usual sources of error in connection with the iodine method, and at the same time greatly increases the speed of the determination. Fig. 114 shows the apparatus.

*A*. 30-cc. Erlenmeyer flask.
*B*. Connection with reduced pressure line from liquid carbon dioxide cylinder.
*C*. Glass manifold.
*D*. Exit connection to trap.
*E*. Water trap to prevent escape of HCl fumes and to prevent air from backing into the flask.
*F*. Cooling tank.
*G*. Low-pressure water wash-out manifold.
*H*. Perforated feed pipe to water cooler.
*K*. Outlet for cooler.
*L*. Electric hot plate.
*M*. Lead drain pipe.

## VOLUMETRIC METHOD FOR TIN IN ALLOYS

The titration of stannous solutions by iodine may be represented by the following reaction:

$$SnO + 2I + H_2O = SnO_2 + 2HI.$$

Sn is equivalent to O or to 2H, hence a normal solution contains one-half the molecular weight of Sn, or 59.35 grams per liter of solution.

**Apparatus.** — This consists of a 300 cc. Erlenmeyer flask, with a one-hole stopper, through which passes a quarter-inch glass tube dipping in a 65 cc. test tube, which it supports by means of a wire as shown in Fig. 115. In place of the test tube a 150 cc. beaker may be used, and a rubber tube 12 to 15 inches in length, one end connected with the apparatus and the other connected with 2–3 inches of glass tubing, which dips in the beaker containing a bicarbonate of sodium solution.

**Reagents.** — O.1N. iodine solution. Standardize against a sodium arsenite (arsenious acid) solution. 1 cc. O.1N I = 0.005935 g. of Sn.

Starch solution. Sulphuric and hydrochloric acids. Antimony powder.

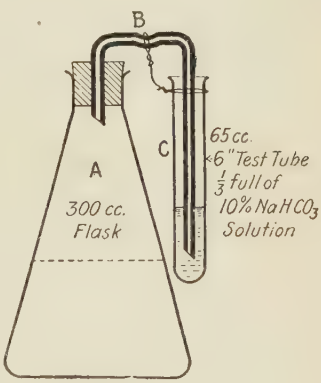


Fig. 115.

**Procedure.** — *Decomposition of the Sample.* Tin alloys generally decompose in hydrochloric acid, but more readily in strong, hot sulphuric acid.

A factor weight 0.5935 gram of the tin alloy is placed in a 300 cc. Erlenmeyer flask and 10 cc. of strong sulphuric acid added. The mixture is heated, preferably over a free flame, until the alloy completely disintegrates. Nearly all of the excess of free acid is expelled keeping the flask in motion over the flame to lessen the tendency towards bumping, which is apt to occur during the concentration. The moist residue is allowed to cool.

100 cc. of (air free) water are added followed by 50 cc. of strong hydrochloric acid and the mixture gently warmed until the solution begins to clear. The apparatus is now assembled as shown in the figure, about 15 cc. of 10% (saturated solution) sodium bicarbonate being placed in the test tube (or 50 cc. in the beaker, if this is preferred to a test tube).

About 1 gram of very finely powered antimony metal is placed in the flask, followed by 10 cc. of saturated sodium bicarbonate solution, the stopper being removed during the addition and then immediately replaced. The air is displaced by the $CO_2$ generated.

The apparatus is now placed on a hot plate, or on an inverted sand bath dish over a flame, and the solution is gently boiled for 10 to 15 minutes. The antimony should be of such fineness as to remain suspended during the ebullition of the liquid at this stage.

The test tube is now nearly filled with saturated sodium bicarbonate and the apparatus removed to a desk for a few minutes, and then placed in a cold water bath of running water or under tap water, until the solution cools down to near room temperature. During this cooling carbonate will be sucked back into the flask " A " to establish pressure equilibrium, $CO_2$ being generated in the flask. Sufficient solution will remain in the test tube to act as a seal and prevent admission of air, which would spoil results by its oxidation of the tin.

The tube B and the test tube C are disconnected, and 5 cc. of starch solution added by means of a pipette, passing through the hole in the stopper (which should be loosened in the throat of the flask).

Standard iodine solution is now added, the tip of the burette passing through the hole of the stopper, agitating the solution by a " swirling " motion of the flask. The end-point is a blue color, which does not fade on stirring the solution.

If a factor weight has been taken, each cc. of the iodine of 0.1N strength is equivalent to 1 per cent of tin.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS

### BICHLORIDE OF TIN

Bichloride of tin is of great importance in some of the industries, especially the textile. It is necessary to have exact analytical control of the processes in which this compound is used in order to insure uniform results and to certify the efficiency and economy of the process. Several methods have been developed for this purpose. The ones given below have had practical application and have proven to be satisfactory.

**Stannic Acid Method. Hot-water Precipitation.** — In the textile industry where bichloride of tin is used, the efficiency of the process depends directly on the neutrality of the tin liquor. If there is more than enough chlorine present in the bichloride solution to exactly oxidize all the tin to the stannic form, this excess is called "free HCl." If there is not enough chlorine present to do this, the deficiency is spoken of as "basic HCl." The difficulty of determining the "free" or "basic" HCl is apparent when it is known that $SnCl_4$ readily decomposes in water, liberating free acid. The following method has been developed especially for this purpose and has given good results.

The important point in this analysis is to determine whether the liquor has "free" HCl present or whether it is "basic" in nature. It has been found that hot water precipitates tin from the $SnCl_4$ solution as stannic hydroxide and at the same time liberates the chlorine as free HCl.

$$SnCl_4 + 4H_2O = Sn(OH)_4 + 4HCl.$$

The $Sn(OH)_4$ separates in a colloidal precipitate which may be filtered off and the tin estimated as $SnO_2$. The liberated acid may be determined in the filtrate, and from this data the "free" or "basic" HCl can be calculated.

**Procedure.** – For accurate work about 20 grams of the liquor should be weighed out in a tared weighing bottle, but for works control, where time is an important factor, it is sufficiently accurate to get the specific gravity of the liquor by means of a hydrometer and take a measured quantity for a sample, calculating the weight from these data.

Transfer the sample to a 100 cc. volumetric flask. Make up to volume with cold distilled water. Draw out of this solution 10 cc. (approximately 2 grams) and place in a 150 cc. tall beaker. Fill the beaker nearly full with boiling hot water, stirring continuously while the water is being poured in. Place the beaker on top of the steam bath and allow the precipitate to settle. Decant the liquor through an 11 cm. 590 S. &. S. filter and wash the precipitate six

times by decantation, using hot water. Now transfer the precipitate to the filter and continue the washing until 1 drop of the filtrate gives no test for chlorine. After most of the water has drained out of the filter, place the paper and precipitate in a tared silica crucible. If there is plenty of time, dry the contents of the crucible on an asbestos board over a low Bunsen flame. In case the analysis must be made in a hurry, cover the crucible and heat it very carefully over a low flame until all the water has been driven out and the paper has been charred. Then remove the cover and increase the heat to the full Bunsen flame and finally blast to constant weight. Weigh as $SnO_2$. Titrate the filtrate with N/1 NaOH, using methyl orange as the indicator.

*Calculation:*

$SnO_2 \times .7877 = Sn$ $Sn \times 2.1945 = SnCl_4$ $SnCl_4 - Sn = Cl$ equiv. to $SnCl \times 1.0282 = HCl$ equiv. to Sn.

$$\frac{HCl}{\text{Weight of sample}} = \text{per cent of HCl equiv. to Sn}$$

$$\frac{\text{cc. of N/1 NaOH} \times .03646}{\text{Weight of sample}} = \text{per cent of HCl (actual).}$$

The difference between these last two figures equals "free" or "basic" HCl.

**The Acker Process Method.** — The theory of this method is practically the same as that of the hot-water method, except that in this case the liberated acid is neutralized with ammonia before the stannic hydroxide has been filtered off, the advantage being that any solution of the stannic hydroxide, by either acid or alkali, is prevented. The method is not applicable for the determination of "free" or "basic" HCl.

**Procedure.** — Weigh out 25 cc. of the bichloride of tin solution. Transfer to a 500 cc. flask (volumetric) and make up to volume with cold water. With a standardized pipette transfer 25 cc. of this solution to a No. 4 beaker. Dilute with hot water to precipitate most of the tin as stannic hydrate. Add 10 drops of phenolacetolin (1 gram of phenolacetolin dissolved in 200 cc. of water). Titrate very carefully with dilute ammonia until the appearance of a rose-red color. Boil a few minutes on the hot plate. Allow the tin precipitate to settle. Decant through an 11 cm. filter paper. Wash rapidly with hot water without allowing the precipitate to cake down in the filter until the washings are free from chlorine. Dry the precipitate in an oven at 100° C. When dry, invert the filter into a tared porcelain crucible and heat on a gauze until the paper has disappeared. Remove the gauze and heat with the full Bunsen flame for a few minutes. Finally blast to constant weight. Weigh as $SnO_2$.

Take the filtrate and washings and dilute them to a volume of 1000 cc. Warm 500 cc. of this solution and saturate it with hydrogen sulphide. If any tin separates, filter and ignite in a tared porcelain crucible. Moisten with a little nitric acid and heat very slowly to drive out the acid. Ignite to constant weight. Weigh as $SnO_2$. Add this result to the $SnO_2$ obtained above when calculating the final result.

### Determination of Tin in Bichloride of Tin as Sulphide

This method is given as an alternative for the Acker Process Method and may be used as a check on that process. Uniform and concordant results have been obtained by the use of the two methods.

**Procedure.** — Weigh out 25 cc. of bichloride and dilute to 500 cc. volume with cold distilled water. Take 25 cc. portions of this solution for analysis. Dilute the sample to 250 cc. Saturate with hydrogen sulphide. Warm the mixture on a hot plate at a temperature of about 65° C. until the precipitate is coagulated. Test the clear supernatant liquor for unprecipitated tin by adding a little hydrogen sulphide water. Filter on an ashless filter and wash free from chlorides. Make the filtrate and washings up to 1000 cc. volume for further determinations. Dry the tin sulphide precipitate on the filter in an oven at 100° C. Remove the precipitate from the paper as completely as possible. Ignite the paper in a weighed porcelain crucible. Cool and add a few drops of nitric acid. Repeat the ignition, heating very carefully at first until the acid has nearly all been driven out. Now place the main tin precipitate in the crucible. Cover, heat gently for a few minutes, moisten with fuming nitric acid, ignite very carefully for one-half hour and then blast for fifteen minutes. Weigh as $SnO_2$.[1]

[1] Much of this chapter was contributed by B. S. Clark, Research Chemist, American Can Company.

## TITANIUM

**Ti, at.wt. 48.1; sp.gr. 4.5; m.p. 1795° C. (15°); oxides TiO, $Ti_2O_3$, $TiO_2$, TiO**

By far the most important application of titanium at the present time is the use of ferrotitanium in the iron and steel industry. The function of the titanium is to deoxidize the steel and consequently to yield a product free from blow-holes and segregation of impurities.

Next in importance is the application of titanium compounds to the textile industry. For use as a mordant in dyeing, and for bleaching or discharging colors.

Titanium compounds are also used for electric light filaments, arc carbons, ceramics, fine brown glazes, paint for iron and steel, etc.

### OCCURRENCE

The element is widely distributed in minerals, soils, clays and titaniferous iron, $FeTiO_3$. It is found in granite, gneiss, mica, slate, syenitic rocks, granular limestone, dolomite, quartz, feldspars and a large number of other minerals. The principal commercial minerals are:

**Rutile,** *Nigrine,* $TiO_2$, is a brownish-red to nearly black, brittle, opaque to transparent mineral, with adamantine to nearly metallic lustre; streak, white to pale brown; hardness 6–6.5. The crystals intrude in other minerals in hair-like filaments. Coarse crystals are found imbedded in quartz, feldspar and other minerals. With iron it is found in black masses.

*Ilmenite,* $FeTiO_3$, containing about 52.7% $TiO_2$.

*Titanite,* $CaTiSiO_5$, containing 34 to 42% $TiO_2$.

*Perovskite,* $CaTiO_3$, containing about 60% $TiO_2$ and 5 to 6% $Yt_2O_3$.

Titaniferous ores of variable titanic oxide content.

### DETECTION

The powdered ore is fused with potassium bisulphate, $KHSO_4$, until effervescence ceases. The cooled mass is dissolved in dilute sulphuric acid by boiling. *Hydrogen peroxide*, $H_2O_2$, added to this titanium solution, produces a yellow to orange color, according to the amount of titanium present. Hydrofluoric acid, or fluorides, destroys the color. Vanadium also produces this color with hydrogen peroxide, but the color is not destroyed by HF. The yellow color, according to Weller is due to $TiO_3$ formed.

*Morphine* produces a crimson color with solutions of titanium in sulphuric acid.

*Zinc* added to hydrochloric acid solutions of titanium produces a blue color, tin a fine violet solution.

If *sulphur dioxide*, $SO_2$, is passed into the solution of titanium to reduce the iron, and the slightly acid solution then boiled, yellowish white metatitanic acid, $TiO(OH)_2$, is precipitated.

**Bead Test on Charcoal.** — A small portion of the powdered mineral heated on charcoal with microcosmic salt and tin produces a violet-colored bead if titanium is present.

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

A knowledge of the solubility of the element and its oxides is of value in the solution of the sample.

**Element.** — This is feebly soluble in cold dilute hydrochloric, or sulphuric acids; more readily so when the acids are heated. It is soluble in cold, concentrated hydrochloric acid; readily soluble in hot, concentrated hydrochloric, or sulphuric acids. It is scarcely acted upon by nitric acid, but readily dissolves in hydrofluoric acids. It is soluble by fusion with the alkalies.

**Oxides.** — $Ti_2O_3$ is soluble in concentrated hydrochloric or sulphuric acids; forming, in the latter case, a violet-colored solution. The oxide is insoluble in water and in ammonium hydroxide.

$TiO_2$ is difficultly soluble in concentrated sulphuric acid, less soluble if strongly ignited. The metatitanic acid, $TiO(OH)_2$, requires strong hydrochloric or sulphuric acid to effect solution, the orthotitanic acid, $Ti(OH)_4$, however, is readily soluble in hot or cold, dilute and concentrated acids. From titanic solutions orthotitanic acid is precipitated by ammonia, the precipitation being assisted by warming. Boiling a slightly acid solution precipitates the metatitanic acid, $TiO(OH)_2$. $TiO_2$ is soluble upon fusing with alkalies. $TiO_2$ is soluble in hydrofluoric acid, forming $TiF_4$, which is volatile, unless an excess of sulphuric acid is present (distinction from silica). The ignited oxide is best dissolved by fusion with $KHSO_4$ and heating the fused mass with dilute sulphuric acid solution. Titanous oxides have a black or blue color.

**Salts.** — Many titanic salts are decomposed in the presence of water, precipitating titanic acid, the extent of the decomposition depending on the quantity of water used. Titanic sulphate is readily soluble in water, and the solution is remarkably stable unless largely diluted with water. Some of the double salts are readily soluble and their solutions stable, i.e., potassium titanium oxalate.

**Solution of Steel.** — The sample may be dissolved in hydrochloric acid (1 : 2). If a residue remains it is treated with a mixture of equal parts of hydrofluoric and sulphuric acids and a few drops of nitric acid, in a platinum dish, and the mixture evaporated to sulphuric anhydride fumes and to complete expulsion of hydrofluoric acid. The colorimetric procedure is now used for estimating titanium.

Note. Titanium in steel treated with ferro carbon-titanium exists in two conditions: (1) Titanium soluble in hydrochloric acid. (2) Titanium insoluble in hydrochloric acid. Of the very small amount of titanium in treated steel the greater part will usually be found in the second form. When the amount of titanium in the steel is exceedingly small, the soluble titanium frequently exceeds the insoluble, and it is then occasionally desirable to determine also that existing in the second form.

**Alloys.** — These are dissolved in concentrated nitric acid, aqua regia or a mixture of the dilute acids. Should nitric acid be used, the excess is expelled by evaporation to dryness with hydrochloric acid. The metals of the hydrogen sulphide group are removed in an acid solution by precipitation with $H_2S$, and titanium determined colorimetrically in the filtrate.

**Ores.** — One to 5 grams of the ore are treated with 10 to 50 cc. of a mixture of sulphuric and hydrofluoric acids (1 to 5), a few drops $HNO_3$ added, and the solution evaporated to fumes to expel HF. If a residue remains upon taking up with water containing a little sulphuric acid, it is filtered off and fused with $KHSO_4$ as directed under the fusion method.

**Fusion Method for Ores.** — The finely powdered sample is fused with four to five times its weight of potassium bisulphate, $KHSO_4$ and the cooled fusion dissolved with dilute sulphuric or hydrochloric acid. In the presence of silica potassium fluoride is added to assist in the decomposition of the material.

**Titaniferous Slags.** — One-half gram of the finely ground sample is decomposed in a platinum dish by a mixture of 5 cc. water, 5 cc. of concentrated sulphuric acid, 2 cc. nitric acid, and 10 cc. of hydrofluoric acid, the reagents being added in the order named. The solution is evaporated rapidly to $SO_3$ fumes to expel fluorides and the excess sulphuric acid until the residue is left nearly dry. After cooling it is taken up with 40 cc. of dilute hydrochloric acid (1 : 3), which will give a clear solution containing all the constituents of the slag except silica, which has been volatilized as $SiF_4$. The solution is diluted to 200 cc. with cold water. Iron and titanium are precipitated by ammonia in slight excess and filtered at once without boiling. The precipitate is dissolved in cold dilute hydrochloric acid and reprecipitated with ammonia. Titanium is now separated from iron by reducing iron with $SO_2$ and precipitating titanium from a boiling acid solution.

### Determination of Titanium when Interfering Elements are Present

If chromium, vanadium or molybdenum is present in the steel, fuse the residue insoluble in hydrochloric acid or the calcined phenylhydrazine precipitate containing the interfering element with a mixture of sodium carbonate and a little sodium nitrate.

Dissolve the fusion in water and filter. The residue on the filter will contain the titanium, free from interfering element. Bring the residue into sulphuric acid solution by methods before described and determine the titanium as usual.

Details of the isolation of titanium are given in the methods for its estimation.

**Separation of Titanium from the Alkaline Earths, etc.** — The hydroxide is precipitated when a titanium solution containing ammonium chloride is treated with ammonium sulphide, whereas barium, strontium, calcium and magnesium remain in solution. Titanium hydroxide may be precipitated by making the solution containing titanium slightly ammoniacal with $HN_4OH$.

**Separation from Copper, Zinc, Aluminum, Iron, etc.** — Titanium is precipitated from a slightly acid solution by boiling, passing sulphur dioxide through the solution to keep the iron reduced and prevent its precipitation.

**Separation from the Bivalent Metals, Manganese, Nickel, Cobalt, Zinc.** — Titanium is precipitated along with aluminum and iron by hydrolysis of its acetate in a hot, dilute solution, whereas manganese, nickel, cobalt and zinc remain in solution.

**Separation of Titanium from Aluminum.** — Small amounts of titanium from large amounts of aluminum. (One part of Ti to 50 parts of Al.) Cupferron, $C_6H_5(NO)N \cdot ONH_4$ added to a decidedly acid solution containing titanium and aluminum precipitates titanium, but not aluminum. The precipitate is washed by decantation and then on the filter with very dilute hydrochloric acid to remove traces of aluminum. The procedure affords a separation of titanium from chromium, nickel, cobalt, manganese, etc. Copper and iron, however, precipitate with the titanium, if present in the solution. The yellow titanium salt has the composition $[C_6H_5(NO)NO]_4Ti$.

**Separation of Titanium from Iron.** - See Gravimetric Method for Determination of Titanium, Modified Gooch Method.

## GRAVIMETRIC METHODS

### DETERMINATION OF TITANIUM BY MODIFIED GOOCH METHOD

This method is applicable to minerals and metallurgical products that are comparatively high in titanium. The method provides for the separation of titanium from iron and from aluminum and phosphoric acid with which it commmonly occurs. The procedure as proposed by F. A. Gooch and modified for non-aluminous rocks by Wm. M. Thornton has been found by the author to give reliable results. The details of the method with a few slight changes found to be advantageous are given below. Iron is separated from titanium by precipitation as a sulphide in presence of tartaric acid, the organic acid is destroyed by oxidation and titanium precipitated from a boiling acetic acid solution. In the presence of alumina and phosphoric acid the impure precipitate is fused with $Na_2CO_3$ and the impurities leached out with boiling water. In presence of zirconium, titanic acid is incompletely precipitated.

**Procedure. Preparation of the Sample.** — *Ores High in Silica.* These may be decomposed by taking to $SO_3$ fumes with a mixture of 10 to 15 cc. of 50% hydrofluoric acid, HF, and 3 to 4 cc. of concentrated sulphuric acid per gram of sample.

**Oxides.** — Decomposed by fusion with sodium or potassium bisulphate. The fusion is dissolved in 10% sulphuric acid, keeping the volume as small as possible. The sample should contain not over 0.2 gram of titanium.

**Precipitation of Iron.** — To the solution containing titanium, tartaric acid, equal to three times the weight of the oxides of titanium to be held in solution, is added. This should not exceed 1 gram of the organic acid, as the subsequent removal of larger amounts would be troublesome. $H_2S$ is passed into the solution to reduce the iron and $NH_4OH$ added to slight alkalinity followed by a further treatment with $H_2S$ to completely precipitate FeS. The solution should be faintly alkaline (litmus) otherwise more ammonia should be added. After filtration and washing of the ferrous sulphide with very dilute and colorless ammonium sulphide, the titanium is entirely in the iron-free filtrate.

**Oxidation of the Tartaric Acid.** — Since titanium cannot be precipitated by any reagent in the presence of tartaric acid, the organic acid is oxidized by addition of 15 to 20 cc. of concentrated sulphuric acid to the sample placed in a 500 cc. Kjeldahl flask. The solution is evaporated to incipient charring of the tartaric acid. After cooling slightly, about 10 cc. of fuming nitric acid are added cautiously, a few drops at a time, and when the violent reaction has subsided the flask is heated gradually (hood), a vigorous reaction taking place accompanied by much effervescence and foaming with evolution of

copious brown fumes. The organic matter gradually disappears, the effervescence becomes steady and finally ceases and white fumes of $SO_3$ are given off. The solution is cooled and the pale yellow syrup poured into 100 cc. of cold water, the flask washed out, adding the rinsing to the main solution. If cloudy, the solution is filtered.

**Precipitation.** — Ammonia is added until the solution is nearly neutral, a point where the solution is slightly turbid, the precipitate dissolving upon vigorous stirring. If a trace of iron is suspected about 1 cc. of 10% ammonium bisulphate is added. Five cc. of glacial acetic acid followed by 15 grams of ammonium acetate or its equivalent in solution is added and the volume of the solution made up to about 350 cc. The solution is brought rapidly to boiling and maintained in ebullition for about three minutes. The titanium will precipitate in white flocculent and readily filterable condition. The precipitate is washed first with water containing acetic acid and finally with pure water. The filter and the precipitate are ignited cautiously over a low flame and finally blasted over a Meker blast for twenty minutes. The residue is weighed as $TiO_2$.

In the presence of large amounts of alumina and phosphoric acid, the residue above obtained is fused with sodium carbonate in a platinum dish and the fusion leached by boiling with pure water. Alumina and phosphoric acid go into solution as soluble sodium salts and titanium oxide remains insoluble in the residue.

Ignited insoluble residue = $TiO_2$.

Note. Titanium may be separated from aluminum by fusing the residue with potassium acid sulphate, $KHSO_4$, and precipitation of titanium in an acid solution by cupferron. $Al_2O_3$ is in solution.

## DETERMINATION OF TITANIUM IN FERRO-CARBON TITANIUM. GRAVIMETRIC METHOD

Into a 6 in. porcelain evaporating dish weigh 0.6 gram (factor weight) of alloy.

Dissolve in a mixture of 15 cc. of dilute sulphuric acid (one acid to one water), 5 cc. of nitric acid, and 10 cc. of hydrochloric acid. Evaporate to fumes of sulphuric anhydride.

Cool and take up by boiling with 50 to 60 cc. of water and 5 to 10 cc. of hydrochloric acid. Filter into a 500 cc. beaker and wash the residue with hot water and dilute hydrochloric acid.

In the filtrate precipitate iron and titanium by ammonia in slight excess. Filter without boiling and wash precipitate twice on filter with hot water.

Reject filtrate. Dissolve the precipitate in a very little dilute hydrochloric acid, washing the filter with hot water and collecting the solution and washings in the original beaker.

Nearly neutralize the solution with ammonia or ammonium carbonate; dilute to 300 cc.; saturate with sulphur dioxide gas, and boil until titanic acid is precipitated and the solution smells faintly of sulphur dioxide.

Filter and wash with hot water and dilute sulphurous acid.

Dry, ignite, and weigh as titanic oxide.

Since the factor weight of sample has been used, one milligram of titanic oxide is equal to 0.1% of metallic titanium.

## VOLUMETRIC METHODS

### THE DETERMINATION OF TITANIUM BY REDUCTION

#### Addition of Ferric Salt and Titration of Reduced Iron with Potassium Permanganate

**Principle.** — Titanic acid is reduced by means of zinc, an excess of ferric sulphate is added and the ferrous salt, formed by reduction by titanous salt, is titrated with standard permanganate. The method is more accurate than direct titration of the titanous salt with permanganate.

**Reaction.** $Ti_2(SO_4)_3 + Fe_2(SO_4)_3 = 2Ti(SO_4)_2 + 2FeSO_4$,
or $TiCl_3 + FeCl_3 = TiCl_4 + FeCl_2$.

#### Preparation of the Sample

**Procedure.** — One to 2 grams of the ore is decomposed by hydrofluoric and sulphuric acids or by fusion with potassium bisulphate or a combination of the two according to the methods already described. Members of the $H_2S$ group, if present, may be removed by $H_2S$. If iron is present it may be determined by boiling off the $H_2S$ in the filtrate containing Fe, Ti, etc., and allowance made in the titration for titanium. If other interfering elements are present in this filtrate, titanic acid may be precipitated by boiling the slightly acid solution (sulphurous acid) according to directions given in the gravimetric method. The washed oxide is dissolved in strong $H_2SO_4$ and diluted as directed below.

**Reduction.** — The solution is washed into a 100 cc. flask and diluted with water so that it will contain 10% of sulphuric acid. This acid holds titanic acid in solution and at the same time is insufficient to oxidize the reduced titanium oxide. Sufficient zinc to cause complete reduction is added and a rubber stopper carrying a Bunsen valve tube and a thistle tube with glass stop-cock is inserted in the neck of the flask. The evolved hydrogen expels the air and reduces the titanic oxide to the titanous form. Iron if present is also reduced. Gentle heat is applied until the excess of zinc dissolves. The solution is cooled and an excess of ferric sulphate added through the thistle tube, followed immediately by cold distilled water until the flask is filled to the neck. The contents of the flask is poured into a No. 6 beaker containing 150 to 200 cc. of cold distilled water and the ferrous iron, formed by the reducing action of titanous salt, is titrated with N/10 $KMnO_4$ solution.

One cc. of N/10 $KMnO_4$ = 0.00481 gram of Ti, or 0.00801 gram of $TiO_2$.

## VOLUMETRIC METHOD BY REDUCTION OF TITANIUM AND TITRATION WITH A FERRIC SALT

The following volumetric method recommended by the Titanium Alloy Mfg. Co., is essentially that described by P. W. &. E. B. Shimer, Proceedings of Eighth International Congress of Applied Chemistry, the method hereafter described differing principally in the form of reductor and also in a few details of operation.

**Reagents.** — Standard ferric ammonium sulphate solution.

Dissolve 30 grams of ferric ammonium sulphate in 300 cc. of water acidified with 10 cc. of sulphuric acid; add potassium permanganate by drops as long as the pink color disappears, to oxidize any ferrous to ferric iron; finally dilute the solution to 1 liter.

Standardize this solution in terms of iron. The iron value multiplied by 1.4329 gives the value in titanic oxide ($TiO_2$); and the iron value multiplied by 0.86046 gives the value of the solution in terms of metallic titanium.

**Indicator.** — Saturated solution of potassium thiocyanate.

**Reductor.** — As a reductor a 500 cc. dispensing burette is used. The internal dimensions of the burette are $1\frac{5}{8}$ by 22 ins.

The reductor is charged with 1200 grams of 20 mesh amalgamated zinc, making a column about 12 ins. high and having an interstice volume of about 135 cc. This form of reductor is convenient, and when used as hereafter described is adapted to maintaining hot solutions, which is essential for complete reduction of the titanium.

The reductor is connected to a liter flask for receiving the reduced titanium solution, through a three-hole rubber stopper which carries also an inlet tube for carbon dioxide supply, and outlet tube for connecting with the suction pump.

**Procedure. Determination of Titanium in Ferro Carbon Titanium.** — One-half gram of sample is dissolved in a 6 in. porcelain evaporating dish in a mixture of 10 cc. of water, 10 cc. of sulphuric acid, 5 cc. of hydrochloric acid, 5 cc. of nitric acid.

The solution is evaporated to fumes of sulphuric anhydride; taken up by boiling with 50 cc. of water and 10 cc. of hydrochloric acid; filtered and washed with hot water and hydrochloric acid.

The filtrate and washings should be about 100 cc. in volume.

The reductor is prepared for use by first passing through it a little hot dilute sulphuric acid followed by hot water, finally leaving sufficient hot water in the reductor to fill to the upper level of the zinc.

The hot titanic solution prepared as described above is now introduced, about 100 cc. of water being drawn from the reductor into the original beaker to bring the solution to about the upper level of the zinc. The water thus removed will not contain any tita-

nium if the operation has been conducted as described; but it serves as a safeguard and is also *convenient* to acidify this water with 10 cc. of sulphuric acid and reserve it on the hot plate to be used as an acid wash after the reduction of the sample solution.

The titanium solution is allowed to remain in the reductor for ten minutes.

While the solution is being reduced the receiving flask is connected to the reductor and the air completely displaced by carbon dioxide, conveniently drawn from a cylinder of the liquefied gas.

When the reduction is complete the receiving flask is connected with the suction pump, and while still continuing the flow of carbon dioxide the reduced solution is drawn out, followed by the reserved acid wash and then three or four 100 cc. washes with hot water. The displacement of the sample solution and washing of the zinc is so regulated by means of the stop-cock that the reductor is always filled with solution or water to the upper level of the zinc.

When the washing is complete, gradually release the suction to prevent air being drawn back into the receiving flask.

Disconnect the flask, add 5 cc. of potassium thiocyanate solution as indicator and titrate immediately with standard ferric ammonium sulphate solution, adding the solution rapidly until a brownish color is produced which will remain for at least one minute.

The method is also well adapted for determining titanium in other titanium products, suitable means being employed for bringing the titanium into sulphuric acid solution.

## COLORIMETRIC DETERMINATION OF TITANIUM WITH HYDROGEN PEROXIDE

**Preliminary Considerations.** — Hydrogen peroxide added to acid solutions of titanium produces a yellow to orange color, the depth of the color depending upon the amount of titanium present. Upon this fact the method is based. It is of especial value in determining small amounts of titanium, as it is possible to detect less than one part of the metal per hundred thousand parts of solution. Color comparisons can best be made on samples containing 0.05 to 5 milligrams of the element; larger amounts produce too deep a color for accurate comparison.

The following interferences should be made note of, e.g., molybdenum, vanadium and chromium also produce a color that would lead to error. Iron present to the extent of 4% or over produces a color that must be allowed for; e.g., 0.1 gram of $Fe_2O_3$ in 100 cc. of solution is equivalent to about 0.2 gm. of $TiO_2$ oxidized by $H_2O_2$ in 100 cc. of solution. Fluorides destroy the color, hence must be absent. Phosphoric acid and alkali sulphates have a slight fading action, hence must be allowed for by adding equivalent amounts to the standard if they are present in the sample. The addition of an excess of sulphuric acid partly counteracts the action of phosphates or alkali sulphates. The color intensity is increased by increase of temperature, hence the standard and the sample examined should have the same temperature. Since metatitanic acid produces no color with hydrogen peroxide, its formation must be prevented; the presence of 5% of free $H_2SO_4$ accomplishes this.

The procedure is very satisfactory for magnetic or other iron ores. It is fully as accurate as the best gravimetric method and very much more rapid.

**Solutions Required.** *Standard Titanium Solution.* — This may be prepared by precipitations of $TiO_2$ from $K_3TiF_6$ according to the gravimetric procedure and purification by solution and reprecipitation, the fluorine being first removed by taking the compound to fumes with $H_2SO_4$ and then hydrolyzing titanium with $NH_4OH$. The washed precipitate is ignited over a Meker flame for fifteen minutes, cooled in a desiccator and placed in tightly stoppered bottle, since $TiO_2$ is slightly hydroscopic.

0.5 gram of $TiO_2$ is fused with about twenty times its weight of $KHSO_4$ in a platinum dish, keeping at fusion heat until the oxide has dissolved. A high temperature is not advisable. The fusion is dissolved in 5% sulphuric acid by gently heating. The solution washed into a 500 cc. graduated flask is made up to volume with 5% $H_2SO_4$. One cc. contains 0.001 gram $TiO_2$, or 0.0006 gram Ti.

*Hydrogen Peroxide.* — Thirty per cent solution. If this is not available sodium peroxide dissolved in dilute sulphuric acid will do.

**Apparatus.** — Colorimeter — See Fig. 85 in the chapter on Lead.

**Preparation of the Sample.** — The solution of the sample having been obtained by one of the procedures given under Preparation and Solution of the Sample, the element may be determined according to the procedure given below. If interfering substances are present, e.g., comparatively large amounts of iron, or if tungsten, vanadium or chromium are present it will be necessary to precipitate titanic acid by adding ammonium hydroxide to the boiling solution as directed under the gravimetric determination of the element. The washed precipitate is dissolved in sulphuric acid.

**Procedure.** — The sulphuric acid solution of titanium should contain 5% of free sulphuric acid. It is poured from the beaker in which solution was effected into a 100 cc. Nessler tube, 2 cc. of hydrogen peroxide, 30% solution, are added and the volume made up to 100 cc. with 5% sulphuric acid. The *standard* is prepared by pouring 40 or 50 cc. of 5% sulphuric acid into a second 100 cc. Nessler tube, adding 2 cc. of 30% hydrogen peroxide, $H_2O_2$, followed by sufficient standard titanium solution to exactly match the sample and the solution made up to 100 cc. with 5% sulphuric acid. The titanium solution is added from a burette, noting the exact volume required. From this the percentage of titanium in the sample can readily be calculated. If iron is present in the sample, an equivalent amount should be added to the standard. If a colorimeter is used, a standard should be prepared which is deeper in color than the sample examined. The standard is poured into the comparison cylinder and the two tubes compared. By raising or lowering the plunger (see illustration) the standard solution is forced in or drawn out of the comparison tube. When the colors match, the cc. in the comparison tube will indicate the amount of $TiO_2$ present in the sample. The solution may be mixed by stirring with a platinum spiral.

*Example.* — One-gram sample required 20 cc. of titanium standard solution, 1 cc. of which contained 0.001 gram of $TiO_2$. Then the sample contains $0.001 \times 20 \times 100 = 2\%$ $TiO_2$.

If the colorimeter has been used and 150 cc. of standard made by adding 30 cc. of standard titanium solution and it is found that the column of liquor in the standard comparison tube stands at 85 cc., the calculation would be as follows: 150 cc. contains $30 \times 0.001$ gram $TiO_2$, therefore 85 cc. are equivalent to

$$\frac{85 \times 0.003}{150} = 0.017 \text{ gram of } TiO_2 \text{ per gram or } 1.7\%.$$

For the practical application of the colorimetric method in determining titanium in steel the following procedure is given.

Note. *Separation of Titanium from Iron.*— J. H. Walton, Jr., separates titanium from iron by fusing the finely powdered substance with three or four times as much sodium peroxide, and extracts the fusion with water. The filtrate contains the sodium pertitanate whereas the iron oxide remains on the filter paper. The filtrate is acidified with $H_2SO_4$ until 5% of free acid is obtained and the color of this solution compared with a standard obtained by fusing a known weight of $TiO_2$ with $Na_2O_2$ and extracting and treating with $H_2SO_4$ as in case of the sample.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS
## THE ANALYSIS OF TITANIFEROUS ORES

### Determination of Titanium

Decompose the ore by fusion with potassium bisulphate, dissolving the fusion in water, hydrochloric and sulphuric acids. If an insoluble residue remains, filter it out. Calcine the residue, add a few drops of sulphuric acid and sufficient hydrofluoric acid to dissolve silica, evaporate to fumes of sulphuric anhydride and then heat to redness.

If a residue now remains, bring it into solution directly in acids or fuse with a little potassium bisulphate, etc., finally adding the solution to the main solution obtained as before described.

If desired, the sample of ore can first be partially dissolved in hydrochloric and sulphuric acids, and the insoluble residue then fused with potassium bisulphate or treated with sulphuric and hydrofluoric acids.

Some ores may be completely decomposed by a mixture of nitric, hydrofluoric and sulphuric acids, evaporating to fumes of sulphuric anhydride in a platinum dish to free the solution from nitric and hydrofluoric acids.

The complete decomposition of the sample having been accomplished, the titanium in the solution is determined by either the gravimetric or volumetric methods.

### Determination of Iron in Presence of Titanium

The sample is decomposed as directed under the Determination of Titanium.

The sulphuric acid solution, which should have a volume of 150 to 200 cc., is saturated with hydrogen sulphide gas to reduce the iron, and filtered to separate any precipitated sulphides and free sulphur. The filtrate is collected in a flask fitted with a rubber stopper through which pass two glass tubes, one reaching nearly to the bottom for conducting gas into the solution, the other a short exit tube. Unless the solution after filtration is still highly charged with hydrogen sulphide, more gas should be passed into the solution to reduce any iron that may have been oxidized by the atmosphere during filtration. The excess hydrogen sulphide is now expelled by boiling the solution while passing a current of carbon dioxide.

When the exit gases cease to darken a piece of filter paper moistened with lead acetate solution, the flask is cooled, while still passing the carbon dioxide. When the flask has partially cooled the carbon dioxide is shut off and the flask quickly cooled in running water and immediately titrated with standard permanganate solution.

### Determination of Silicon

This determination is conveniently combined with the determination of iron, the ore being preferably decomposed by fusion with potassium bisulphate. The fusion is dissolved and evaporated with excess sulphuric acid to fumes of sulphuric anhydride and the silica determination finished as usual — weighing, volatilizing with hydrofluoric acid, etc. If the ore contains quartz or a silicate undecomposable by treatment with potassium bisulphate and hydrofluoric acid, the residue filtered from the sulphuric acid solution should be fused with sodium carbonate and the silica then determined as usual.

### Determination of Aluminum

After making determination or separation of titanium by *gravimetric* method, use the filtrate for determination of aluminum.

### Phenylhydrazine Method for Determination of Aluminum in Presence of Iron

The iron and aluminum should be in hydrochloric or sulphuric acid solution. Nearly neutralize the solution with ammonium carbonate. Pass sulphurous acid gas to complete reduction of the iron. Boil until the excess sulphurous acid is driven off and if titanic acid separates filter it out.

After filtering out titanic acid again nearly neutralize with ammonium carbonate, pass a little sulphurous acid gas and heat for a few minutes to reduce any iron that might have been oxidized during filtration. If titanium has not been detected the second treatment with sulphurous acid may be omitted. In either case the solution still containing a little free sulphurous acid is nearly neutralized with ammonium carbonate, diluted to 300 cc. and 3 cc. of phenylhydrazine added. Stir thoroughly, let settle and filter out the alumina. If the precipitate is discolored by iron, dissolve in hydrochloric acid, and repeat the reduction, neutralization and precipitation by phenylhydrazine. Ignite and weigh $Al_2O_3 + P_2O_5$. Since the alumina precipitate may be contaminated by phosphoric anhydride ($P_2O_5$), determine it by analysis and correct the alumina determination accordingly.

### Determination of Phosphorous

Phosphoric acid may be separated from titanic acid by repeatedly fusing the ore with alkali carbonate and extraction of alkali phosphate with water.

The determinations of other constituents of the ore are conducted by the usual methods of ore analysis.

## ANALYSIS OF TITANIUM PIGMENTS[1]

Titanium pigment products consisting of titanic oxide and barium sulphate can be analyzed by the following method.

Weigh a $\frac{1}{2}$ gram sample into a 250 cc. Pyrex glass beaker; add 25 cc. of concentrated sulphuric acid and 4 grams of sodium sulphate. Mix well and heat on a hot-plate until fumes of sulphuric anhydride are evolved and then heat directly over a flame to boiling for five minutes or until solution is complete. Traces of silica, if any, remain as an insoluble residue.

Cool, take up in 150 cc. of water, boil and filter off barium sulphate and silica, washing with 5% sulphuric acid to free residue from titanium, calcine and weigh barium sulphate.

Evaporate the filtrate to 100 cc. and determine the titanium as directed under volumetric method for the determination of titanium.[2]

[1] Method of analysis used in the laboratories of The Titanium Alloy Manufacturing Company.

[2] The Editor desires to acknowledge the assistance received in the preparation of this chapter from L. E. Barton, Chief Chemist of the Titanium Pigment Company, Niagara Falls, N. Y.

## TUNGSTEN

**W., at.wt. 184.0; sp.gr. 18.77; m.p. 3000° C.; oxides, $WO_2$ (brown) $WO_3$ (yellow)$_4$ acids, $H_2WO_4$; ortho tungstic; $H_2W_4O_{13}$, meta tungstic**

### OCCURRENCE

The element is met with in alloys — ferro-tungsten, silico-tungsten, tungsten steels containing as much as 10 to 20% of the metal, used for making high-speed, self-hardening cutting tools; tungsten powder; alkali tungstates for mordanting purposes; tungstic oxide, $WO_3$; tungsten electric light filaments, etc.

Commercial tungsten minerals are marketed usually in the form of concentrates derived from treatment of lean ores by water concentration, or, sometimes, as specially selected high-grade ore which has not been subjected to dressing operations other than hand sorting.

The important commercial minerals are *Wolframite* — iron-manganese tungstate; *Huebnerite* — manganese tungstate; *Ferberite* — iron tungstate; *Scheelite* — calcium tungstate. The first three grade into each other imperceptibly; commercially, they are all classed as Wolframite although the predominant mineral may, in some cases, be either manganese tungstate or iron tungstate. The determinations usually required are tungstic oxide, manganese, tin, phosphorus, sulphur, copper and arsenic, sometimes molybdenum, which occurs more or less frequently in Scheelite, and occasionally bismuth and lead.

The principal minerals associated with tungsten concentrates are pyrite, arseno-pyrites, cassiterite, magnetite, columbite, and always more or less quartz and silicates. Scheelite sometimes is associated with barite.

The following analytical methods have been in practical use for a long time; they have been modified from time to time as experience showed necessary. Many suggestions from Works' chemists and others have been adopted. The descriptions are given in detail where this has been thought to be necessary because much depends upon minor points and upon the experience gained in making many hundreds of determinations.

**Minerals.** *Wolframite*,[1] — $(Fe,Mn)WO_4$, (76% $WO_3$) is a dark gray to black, opaque to translucent, heavy mineral with submetallic to resinous lustre. The crystals are often reddish-brown in color, cleav-

[1] Wolframite is a tungsten mineral, Wulfenite a molybdenum mineral $PbMoO_4$.

able and in granular masses, orthorhombic in appearance, monoclinic. The streak varies from gray, yellowish brown to dark brown; hardness 5–5.5.

*Scheelite*, $CaWO_4$ (80.6% $WO_3$) is white, gray, pale yellow, brown or green in color; it is transparent to opaque; brittle; with a white streak; hardness 4.5–5. The lustre is adamantine. The heavy mineral occurs in masses and square pyramids. Crystallization — tetragonal.

**Suggestion to Students.** — Determine tungsten in steel by the gravimetric method on page 606. Determine tungsten in an ore by the method given on page 610.

## DETECTION

**Minerals.** — The finely powdered material is decomposed by treating with strong acid according to the procedure given on page 610. Tungsten is precipitated with cinchonine, the precipitate filtered off and dissolved in ammonium hydroxide, then acidified with hydrochloric acid and reprecipitated with cinchonine as described.

Tungsten oxide may be confirmed as follows:

1. Then the residue is suspended in dilute hydrochloric acid and a piece of zinc, aluminum, or tin placed in the solution. In the presence of tungsten a blue-colored solution or precipitate is seen, the color disappearing upon dilution with water.

2. A portion of the precipitate is warmed with ammonium hydroxide and the extracts absorbed with strips of filter paper.

(*a*) A strip of this treated paper is moistened with dilute hydrochloric acid and warmed. In the presence of tungstic acid a yellow coloration is produced.

(*b*) A second strip of paper is moistened with a solution of stannous chloride. A blue color is produced in the presence of tungsten.

(*c*) A third strip dipped into cold ammonium sulphide remains unchanged until warmed, when the paper turns green or blue if tungsten is present.

**Iron, Steel and Alloys.** — These decomposed with strong hydrochloric acid followed by nitric acid as directed under Solution of the Sample leave a yellow residue in the presence of tungsten. If this residue is digested with warm ammonium hydroxide and the extract evaporated to dryness a yellow compound, $WO_3$, will remain if tungsten is present. This oxide may be reduced in the reducing flame to the blue-colored oxide.

## METHODS OF ANALYSIS OF TUNGSTEN

### Solution of the Sample

*For solution* of the sample the following facts should be kept in mind regarding solubilities.

The metal is practically insoluble in HCl and in $H_2SO_4$. It is slowly attacked by $HNO_3$, aqua regia and by alkalies. It is readily soluble in a mixture of $HNO_3$ and HF (= $WF_6$ or $WOF_4$).

*Oxides.* — $WO_2$ is soluble in hot HCl and in hot $H_2SO_4$ (= red sol.), also in KOH (red sol.). The oxide $WO_3$ is scarcely soluble in acids, but is readily soluble in KOH, $K_2CO_3$, $NH_4OH$, $(NH_4)_2CO_3$, $(NH_4)_2S_x$. Both the acid and the alkali solutions deposit the blue oxide on standing.

**Acids.** — Ortho tungstates. A few are soluble in water and in acids. The alkali salts are only slightly soluble. The meta tungstates are easily soluble in water. Tungstates are precipitated from alkali salts by dilute $H_2SO_4$, HCl, $HNO_3$, $H_3PO_4$ (aqua) as yellow $WO_3 \cdot H_2O$ or white $WO_3 \cdot 2H_2O$. Meta tungstates are not precipitated by cold acids, but are precipitated by boiling and by long standing.

**Solution of Minerals.** — The material is best decomposed by acid treatment as described on page 610. Use of a fusion as a means of decomposition of tungsten ores preliminary to either the qualitative detection or the quantitative determination of tungsten cannot be recommended. The precipitation of tungsten by boiling with acids in presence of considerable amounts of *alkali salts* (such as result from acidification of a fusion) is absolutely worthless inasmuch as large amounts of tungsten always remain in solution. Repeated evaporations do not improve matters. In fact, when the amount of tungsten present is small, and especially if the ore contains much phosphorus, there is small likelihood that any of the tungsten will be precipitated. The use of cinchonine is necessary in order to completely precipitate tungsten under these conditions.

The methods of analysis make provision for the separation of interfering substances. The following methods of separation of elements that interfere in the analysis are given for reference.

**Separation of Tungsten from Silica.** — The oxide of tungsten, as ordinarily obtained, is frequently contaminated with silica. The removal of silica is accomplished by heating the mixture in a platinum dish with sulphuric and hydrofluoric acids and volatilizing the silica. After taking to dryness and igniting gently, the last traces of sulphuric acid are expelled by adding ammonium carbonate and again igniting.

In presence of small amounts of silica (0.1 to 0.2%) and large amounts of tungsten (75 to 85%) J. A. Holladay recommends evaporation with sulphuric and phosphoric acids, filtration to remove the

bulk of the tungsten, and subsequent ignition and volatilization with sulphuric and hydrofluoric acids.

**Separation from Tin.** — The weighed residue is mixed with six to eight times its weight of ammonium chloride (free from non-volatile residue) in a platinum crucible, placed in a larger crucible, both vessels being covered. Heat is applied until no more vapors of ammonium chloride are evolved. Additional ammonium chloride is added and the treatment is repeated three times. The fourth treatment is followed by weighing of the residue and the treatment repeated once more. If no further loss of weight takes place it is assumed that all of the stannic oxide has been driven off. The inner crucible is now placed directly over the flame and heated to dull redness for a few minutes and the oxide, $WO_3$, weighed.

**Separation from Titanium.** — The material is heated with $K_2CO_3$ and $KNO_3$, tungsten is dissolved out with water and precipitated as mercurous tungstate.

## GRAVIMETRIC PROCEDURES FOR DETERMINING TUNGSTEN

Since there is no highly commendable volumetric procedure for determining tungsten, the gravimetric methods are preferred.

The element is determined as tungstic oxide, $WO_3$. It may be isolated preferably by precipitation with cinchonine, or in the form of tungstic acid, ammonium tungstate, or as mercurous tungstate, in the usual course of analysis, all of which forms may be readily changed by ignition to the relatively non-volatile oxide, $WO_3$.

### Gravimetric Determination of Tungsten in Steel and Alloys

Tungsten alloys may be decomposed by hydrochloric (or sulphuric) and nitric acids. Tungsten precipitates, carrying down chromium and a little iron. The bulk of the iron is filtered off and tungsten determined in the residue, by direct or difference methods.

**Special Reagent. Cinchonine Solution.** — 100 grams of the alkaloid dissolved in dilute (1 : 3) HCl and made to 1000 cc. with the dilute acid. *Wash Solution.* 30 cc. of the above solution, with 30 cc. of strong HCl diluted to 100 cc.

**Procedure. 1. Decomposition of the Sample.** — Two grams of high tungsten alloys or 5 grams of alloys low in tungsten are dissolved in a 350 cc. beaker by addition of 20 cc. of strong HCl, the beaker being placed over an asbestos mat on a hot-plate or steam-bath. (The temperature should be below the boiling point of HCl, since the acid should remain strong to effect decomposition.) Since the reaction is energetic the beaker is covered by a watch glass. Ten cc. of strong nitric acid are added, pouring small portions at a time through the lip of the beaker. The sample is digested until all the black particles have dissolved and only the fine greenish yellow tungstic oxide is evident. Agitation of the liquor to prevent caking assists the reaction.

2. When the sample is decomposed, the beaker is uncovered and the solution evaporated rapidly to about 20 cc. and then cautiously at low heat to about 5–10 cc.; 5 cc. of HCl are added to the moist residue and the solution diluted to about 50 cc. and heated to boiling; 2–3 cc. of cinchonine reagent are added. Avoid taking to dryness and baking as this will make the tungsten difficult to dissolve in $NH_4OH$. See step 4.

3. The mixture is filtered and the ferric chloride washed out from the tungstic residue with dilute HCl (1 : 10), *i.e.*, until the wash solution passes through the filter colorless. The filtrate is tested for tungsten by addition of more cinchonine. See step 7. As small amounts of tungsten come down slowly at least an hour should be given for the test.

4. A clean beaker is placed under the filter and tungsten dissolved out from the impure residue by treating this with warm ammonia water (1:5), the filter being half filled with each washing and thoroughly drained. It is advisable to rinse out the beaker in which the decomposition is made, with warm ammonia solution and pour this on the filter. After five washings the filter is cautiously removed and spread out on a watch glass. The residue is washed into a beaker with a stream of ammonia water and digested with about 20–30 cc. of ammonia for about 5 minutes, warming to near boiling. The solution is poured through a fresh filter into the main extract, the filter is drained and then washed twice more with warm ammonia solution (1:5). All the tungsten should now be in the filtrate. If much residue remains as in case of high silica samples, tungsten is apt to be present. This is recovered by acid sulphate fusion. See Notes.

5. The filtrate is boiled to expel the ammonia. When the odor has become faint, HCl is added until the solution is just acid and about 3 cc. excess is added. The total volume will be 75–100 cc., after boiling. Acidification may cause some tungsten to precipitate but this does no harm. The ammonia is generally expelled by boiling the filtrate down to half its original volume.

6. 10 cc. of cinchonine reagent are added to the hot solution and the mixture stirred and allowed to settle until cold. If the supernatant solution is cloudy, stirring up the precipitate and allowing it to settle will clear the solution. It is well to test the clear liquor with a few drops more of the reagent to ascertain whether all of the tungsten has precipitated.

7. The solution is filtered and the tungsten residue washed three or four times with dilute cinchonine reagent (washing down from the rim of the filter), and once with 5–10 cc. of water.

NOTE. The filtrate from step 3 may contain some tungsten. If the filtrate treated with cinchonine has become cloudy on standing it must be filtered, the residue washed with cinchonine reagent as in the procedure above and the filter and residue added to that containing the bulk of the tungsten.

8. The filter (or filters) is ignited in a weighed crucible to destroy the carbon, then cooled and weighed as $WO_3$.

$$WO_3 \times 0.7931 = W$$

NOTE. The oxide $WO_3$ fused with $KHSO_4$ and the cooled melt extracted with ammonium carbonate reagent should give a clear solution. If the solution is cloudy $SiO_2$ is indicated. This should be filtered off, ignited and its weight subtracted from the $WO_3$ obtained above. See optional below.

The $KHSO_4$ fusion may be made in a porcelain or platinum crucible.

### Optional Method

The impure residue obtained in step 3 of the first procedure is ignited and weighed. The residue is now fused with acid potassium sulphate, $KHSO_4$, (5–6 grams of salt). The heating is continued until effervescence ceases and the mass changes to a clear solution. The fusion is cooled by rotating the crucible so that the mass is spread in a layer over the sides. It is now dissolved by placing in about 100 cc. of ammonium carbonate solution (10% sol.) and heating to boiling. Iron, chromium and silica will remain insoluble, tungsten will be in solution. The liquor is filtered and washed 4 or 5 times with water containing a little $(NH_4)_2CO_3$. The residue is ignited, cooled and weighed. The difference of this weight and that of the impure residue is due to the $WO_3$.

Note. If the carbonate extract is boiled, acidified and cinchonine reagent added, tungsten will precipitate as the cinchonine compound. See Notes.

### Notes

The use of sulphuric acid in place of hydrochloric acid in the decomposition of the sample offers no advantages as to speed of decomposition. On the other hand with sulphuric acid treatment tungsten is invariably found in the filtrate (step 3) while with the HCl method it is seldom found in appreciable amounts.

Hydrofluoric acid assists in the decomposition of alloys high in silicon. A large excess must be avoided as this would attack the glass of the beaker with liberation of silicic acid, and fluosilicic acid. With large amounts of HF a platinum dish should be used.

$WO_3$ does not dissolve readily in ammonia after it has been ignited. The moist residue of tungsten precipitated by acids is easily soluble in ammonia. If an appreciable amount of residue remains from the ammonia extraction, it is fused with $KHSO_4$, extracted with a 10% solution of $(NH_4)_2CO_3$, the $CO_2$ expelled by boiling and the ammoniacal solution filtered from silica, vanadium, iron, etc., and the tungsten precipitated and determined according to the procedure outlined in steps 5 to 8 inclusive.

$SiO_2$ is but slightly soluble in dilute ammonia solution. The silica dissolved by 100 cc. of 1 : 1 $NH_4OH$ in a 30 hour treatment on a 47% $SiO_2$ ore amounted to less than 0.005 g. on a gram sample. With a 30 minute treatment the amount was inappreciable. In case of doubt treat the $WO_3$ with HF in a platinum crucible and again ignite after expelling the acid by evaporation.

### Tungsten in Tungsten Metal and Ferro-Tungsten

Treat one gram of the finely ground sample in a large (60 cc.) platinum crucible fitted with a cover with 5 cc. of HF, add $HNO_3$, drop by drop, until the metal dissolves. Add 3–4 cc. of $H_2SO_4$ and evaporate on a steam bath until $HNO_3 + HF$ are expelled. Shake gently over a small Bunsen flame until $H_2SO_4$ fumes strongly. Cool, transfer to a 250 cc. beaker with water, finally wiping the crucible with a little filter paper. A little $WO_3$ sticks to the crucible; it cannot be removed by wiping. Reserve the crucible. Dilute the contents of the beaker to about 150 cc. with water, add 3 cc. of HCl and boil. Remove from the stove and to the hot solution add 5 cc. of cinchonine solution and let stand over night (or at least four or five hours). Filter on "ashless paper" and wash with dilute cinchonine solution. Gently ignite the precipitate in the crucible in which it was originally treated. Heat for five minutes with full Bunsen burner flame, cool and weigh. Add about 5 grams of $Na_2CO_3$ and fuse, running the fusion around the side of the crucible to remove all of $WO_3$. Dissolve the fusion in hot water; filter and wash five or six times with hot water. Place the filter in the crucible and ignite, add a little $Na_2CO_3$ and fuse again. Dissolve the fusion in water, filter and wash *very* thoroughly with hot water to remove last traces of $Na_2CO_3$, ignite in the same dish as at first, cool and weigh. The difference between weight of dish plus residue and weight of dish plus tungstic oxide is $WO_3$.

**Dilute Cinchonine Solution.** — 30 cc. strong cinchonine solution and 30 cc. of HCl to one liter.

**Strong Cinchonine Solution.** — 100 grams of cinchonine dissolved in dilute HCl (1 part of acid: 3 parts of water) and diluted to one liter with acid of the same strength.

## GRAVIMETRIC DETERMINATION OF TUNGSTEN IN ORES AND CONCENTRATES

### Special Reagents

**Cinchonine Solution.** — Cinchonine solution is made by dissolving 100 grams of the alkaloid in dilute HCl (1 part of acid to 3 of water) and diluting to 1000 cc. with HCl of the same strength.

**Cinchonine Wash Solution.** — 30 cc. cinchonine solution, 30 cc. strong HCl to 1000 cc. of water.

### Preparation of the Sample

The ore should be ground in agate to pass a 200 mesh screen; double screening is recommended to insure perfect fineness.

Weigh one gram into a 350 cc. beaker, add 5 cc. of water and shake to spread the ore evenly over the bottom of the beaker. Add 100 cc. of strong HCl, cover the beaker and set it to warm gently for an hour. The temperature should not exceed 60° C. — higher heating expels HCl gas. The ore is slowly decomposed and most of the tungsten is held in solution by the excess of HCl, leaving the undecomposed ore exposed to further attack by the HCl.

Stir the solution with a glass rod once or twice during this digestion to prevent the formation of crusts or cakes on the bottom. The glass rod may be left in the beaker.

After an hour increase the heat and boil until the solution is evaporated one-half or thereabouts. The cover may be removed after boiling begins, or better, it may be supported over the beaker on three glass hooks. After the liquid is reduced in volume to 50 or 55 cc., scrape the bottom of the beaker thoroughly with a glass rod to detach *all* caked ore and residue — this is very important, otherwise complete decomposition by the acid treatment is difficult if not impossible to accomplish. Add 40 cc. more of strong HCl and 15 cc. of $HNO_3$, replace the cover and boil until all danger of spattering (owing to the rapid expulsion of chlorine) is past, remove the cover and evaporate to a volume of 50 cc., then add 5 cc. more of $HNO_3$, replace cover and continue boiling, finally remove cover and evaporate to a volume of 15 cc. or less. All this boiling and evaporation requires about an hour. Occasional stirring to break up crusts, especially when fresh additions of acid are made, is recommended.

Add 200 cc. of hot water to the concentrated solution, stir well and simmer gently just at the boiling point for half an hour. Nearly all the tungstic acid is separated after the addition of nitric acid and during the subsequent simmering and boiling after dilution, but a little may remain in solution. Add 6 cc. of cinchonine solution, stir well and let stand for half an hour, or longer if convenient, thus precipitating all tungsten.

This method of attack is preferable to that formerly employed wherein less acid was used and $HNO_3$ was added earlier in the digestion. Most ores are completely decomposed, so far as tungsten minerals are concerned, but it is unsafe to assume that this is the case unless the residue is pure white silica.

After the tungstic acid residue has settled well and has stood for half an hour, filter the solution through a 9 cm. paper, using a little paper pulp in the filter. Wash the residue well, first by decantation in the beaker and afterward on the paper with a dilute solution of cinchonine and HCl.

It is unnecessary to detach the tungstic acid which adheres to the sides of the beaker, but washing should be thorough to remove all iron, manganese, calcium, etc., from the residue and filter paper. Finally wash both beaker and filter *once* with cold water to displace most of the dilute cinchonine washing solution.

### Procedure for Isolation of Tungsten

Wash the tungstic acid and residue back from the filter into the original beaker with a fine jet of water from a wash bottle — the residue washes out easily because of the paper pulp which prevents adherence — about 25 cc. of water should be used. Add 6 cc. of strong $NH_4OH$, cover the beaker and warm it gently for about ten minutes. Tungstic acid dissolves readily. Stir well and wash down the sides of the beaker with dilute ammonia, make sure that all the yellow tungstic acid has dissolved, then filter the warm solution through the same filter paper that was used at first, thus dissolving the small amount of tungstic acid that adhered thereto. Collect the filtrate in a 400 cc. beaker, wash the original beaker and the filter paper thoroughly with dilute ammonia (1 part strong of $NH_4OH$: 9 parts of $H_2O$). The filtrate should be clear, or at most only slightly cloudy. The addition of about one gram of $NH_4Cl$ to the solution before filtering and the use of a little of the same salt in the wash solution will insure a perfectly clear filtrate; but the use of this salt is not recommended unless the silicious residue tends to pass the filter in large amount. The residue insoluble in ammonia will usually be free from tungsten; it may consist of tin oxide (cassiterite) silica and undecomposed silicates, titanium minerals or columbite; to make sure, it must be fused as described below.

Cover the 400 cc. beaker and boil it until free ammonia is expelled. The object of boiling off the free ammonia is to minimize ammonium salts since the cinchonine tungsten compound to be precipitated comes down more quickly and completely in solutions free from ammonium salts. Dilute the solution to 200 cc. with *hot* distilled water, acidulate with 3 cc. of HCl and add 6 to 8 cc. of cinchonine solution. Stir very briskly for half a minute, which will cause the flocculent precipitate to agglomerate. It will then settle rapidly, leaving a clear supernatant liquid. Let it stand until cold, filter on

an 11 cm. weightless ash filter (B & A. — A grade) which has been treated to a rather copious dose of paper pulp. If ammonium chloride is used in the prior operation, the solution should be allowed to stand for several hours, best over night, after adding cinchonine. Wash well with dilute cinchonine solution (wash solution described above) policing the beaker with a rubber tipped rod. Follow the cinchonine wash by one washing with cold water, transfer the filter to a small weighed platinum dish or large crucible, dry by heating on the hot plate, then burn the filter *slowly* over a bunsen burner or in a muffle followed by strong ignition until all carbon is consumed.

The use of paper pulp in the filter promotes ignition, leaving the ignited precipitate as a *porous*, friable mass, whereas if paper pulp is not used, the ignited precipitate is dense and it is sometimes difficult to burn the carbon completely.

After the carbon is practically all consumed break down the residue with a glass rod flattened at one end, wipe off the end of the rod with a small piece of moistened filter paper, adding it to the dish. Any remaining carbon and the small piece of filter paper are quickly burned, leaving a pure yellow residue.

Moisten the residue with three drops of strong $H_2SO_4$, add 5 cc. of HF and evaporate slowly on the hot plate until the HF is expelled. It is best to continue heating on the hot plate until the $H_2SO_4$ is expelled also; there is then no danger of spitting. Ignite the dish cautiously at first, finally at full red heat for ten minutes, cool in a desiccator and weigh as $WO_3$.

The residue left after the ammonia treatment may in some cases contain $WO_3$, although with Scheelite and most pure ores and concentrates it does not. It is best in all cases to examine it. In the case of impure ores containing much insoluble residue, the residues from duplicate determinations should be examined separately. When the residue is small and light-colored, it suffices to unite the duplicates for this determination.

Ignite the filter containing the residue in a small *porcelain* crucible. This is necessary because tin may be present, which would be reduced by the filter paper and ruin platinum. Mix the ignited residue with five or six times its weight (in any case at least one gram) of sodium carbonate plus a very little $KNO_3$. Transfer the mixture to a platinum crucible and fuse for five or ten minutes. Leach the fusion with 50 cc. of hot water in a small beaker, filter, acidulate slightly with HCl and boil to expel $CO_2$. Add 5 cc. of cinchonine solution. Let the beaker stand for several hours, best over night; long standing is essential because small amounts of tungsten are slowly precipitated by cinchonine in the presence of alkaline chlorides.

If any tungsten precipitate appears, filter it off on a 7 cm. paper and wash it with dilute cinchonine solution, followed by one wash with cold water, dissolve on the filter in warm dilute ammonia, collecting the filtrate in a small beaker, boil out the excess of ammonia.

make slightly acid with HCl and reprecipitate the tungsten with cinchonine. This reprecipitation is done in a very small volume of liquid practically free from salts so that the tungsten comes down quickly, let it stand for an hour, filter on a small low ash filter containing a little pulp, wash with dilute cinchonine solution followed by one wash with water, ignite, cool, treat with a drop of $H_2SO_4$ and 1 cc. of HF, evaporate, ignite and weigh. Add the percentage of $WO_3$ thus found to the principal amount.

**Factors:** $WO_3 \times 0.7931 = W$,
$W \times 2.4739 = PbWO_4$.

### Aqua Regia Method of Watts

One gram of medium grade, or 0.5 gram of high grade, *very* finely pulverized ore, is treated in a 4-oz. flask with 40–50 cc. aqua regia and kept at moderate heat, *below boiling*, on a hot plate, until the solution has evaporated to about 15 cc. The solution is shaken frequently to prevent a solid cake forming at the bottom of the flask, which would prevent complete action of the acid on the ore.

The solution, removed from the hot plate, is diluted to about 50 cc. with hot distilled water and set aside to settle for half an hour. The clear liquor is decanted through a paper filter and the residue washed in the flask twice by decantation with 25 cc. portions of water slightly acidulated with HCl.

The $WO_3$ in the flask is dissolved with 20 cc. of 1 : 5 $NH_4OH$ containing 2–3 drops of HCl. The solution is decanted through the filter and any remaining residue washed by decantation twice with the ammonia reagent.

If the residue is white it is transferred to the filter. If any black particles of undecomposed ore are evident, the residue is again digested with 10–15 cc. of aqua regia and treated as in the first case, only with relatively smaller portions of solutions. The ammonia extract is added to the filter. And the filter washed down in the customary way to remove all tungsten solution, allowing it to flow into the main extract.

The filtrate containing the tungsten is evaporated to dryness in a platinum dish over a water bath. The ammonia salts expelled by heat. The residue cooled is treated with 1–2 drops of $H_2SO_4$ and about 2 cc. of HF. The silica is expelled (in hood), together with the acids by gently heating. The residue is now heated to dull redness for 5–10 minutes, then cooled in a desiccator and weighed as $WO_3$.

### Volumetric Method

Tungsten is isolated as the oxide $WO_3$, and an excess of N. NaOH added. The excess is titrated with N. HCl.[1]

One cc. N. of NaOH = 0.116 gram of $WO_3$, or = 0.092 gram of W.

[1] Messrs. A. M. Smoot and J. A. Holladay have given valuable assistance in the preparation of this chapter.

## URANIUM

**U, at.wt. 238.5; sp.gr. 18.7; m.p. < 1850° C.; oxides $UO_2$, $UO_3$, (oxide $U_3O_8$, formed by ignition = $UO_2 + 2UO_3$)**

The element is used in the ceramic industry for producing yellow, brown, gray, and velvety-black tints. It produces canary-yellow glass. It is used as a mordant in dyeing of silk and wool. It also finds use in photography. The metal is used in cigarette-lighters and self-lighting burners.

### OCCURRENCE

Nearly all the silicates, phosphates and zirconates of the rare earths contain uranium. The element occurs in the following minerals:

*Uraninite,* Pitchblende, 40 to 90% $U_3O_8$, Ca, N, Th, Fe, Bi, Cu, Zn may be present. The mineral is black, brittle, opaque, heavy, gray, olive green or dark brown; hardness 5.5.

*Carnotite,* $(K_2.Ca)O.2UO_3.V_2O_5 \times H_2O$ (structure not definite only approximate as given). The mineral is usually canary yellow in color, sometimes red or black. Loosely cohering masses of minute scales. Rarely compact.

*Autunite,* $Ca(UO_2)_2P_2O_8.8H_2O$, contains 55 to 62% $UO_3$.

*Torbernite,* $Cu(UO_2)_2.P_2O_8.8H_2O$, contains 57 to 62% $UO_3$.

*Samarskite,* a urano-tantalate of iron and yttrium, etc., 10 to 13% $UO_3$.

*Fergusonite,* a columbate of cerium, uranium, yttrium, calcium and iron.

### DETECTION

The mineral is warmed with a slight excess of nitric acid (1:1) until decomposition is complete. The solution is diluted with water and then an excess of sodium carbonate added and the mixture boiled and filtered. Sufficient nitric acid is added to neutralize the carbonate, and after expelling the $CO_2$ by boiling, sodium hydroxide is added to the filtrate. A yellow precipitate is formed in presence of uranium. The precipitate is insoluble in an excess of the reagent, but dissolves in ammonium carbonate.

*Uranous salts* are green or blue and form green or bluish-green solutions, from which alkalies precipitate uranous hydroxide, reddish brown, insoluble in excess, but readily dissolved by ammonium carbonate. Uranous salts are strong reducing agents.

*Uranyl salts* ($UO_2.R_2$) are yellow. Alkali carbonates give a yellow precipitate, soluble in excess. $UO_2$ is regarded as a basic radical, known as "uranyl." The radical migrates to the cathode, upon electrolysis of a uranyl solution. Uranyl salts are more stable than uranous and are better known.

**Potassium ferrocyanide,** $K_4Fe(CN)_6$, added to uranous or uranyl solutions gives a reddish brown precipitate (or a red color in dilute solutions). The precipitate dissolves in a large excess of HCl. If sufficient ferrocyanide is present the color changes to green on boiling. Addition of sodium hydroxide to the ferrocyanide precipitate of uranium changes the color to yellow. (Distinction from cupric ferrocyanide. Ferrocyanide gives a green precipitate with vanadium, the color deepens on addition of nitric acid. A blue color is produced with ferric iron. No color change with chromates. Distinction from vanadium, chromium and iron.)

*Barium carbonate* precipitates the uranic ion completely. (Distinction from the ions of nickel, cobalt, manganese, zinc.)

*Disodium hydrogen phosphate* added to uranyl solutions, in presence of alkali acetates or free acetic acid gives a yellowish white precipitate, $UO_2HPO_4 \times H_2O$, soluble in mineral acids. Warming promotes precipitation.

*Tartaric acid*, certain organic compounds, hydroxylamine hydrochloride, ammonium carbonate prevent precipitation of uranium by alkalies and ammonia.

*Oxides*, $UO_2$, brown or black; $UO_3$, brick red; $UO_2(OH)_2$, yellow. All oxides are converted to $U_3O_8$ on ignition with free access of air.

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

*The element* dissolves in hydrochloric and in sulphuric acids; less readily in nitric acid. It is insoluble in alkaline solutions.

*The oxide*, $UO_2$, dissolves in nitric acid and in concentrated sulphuric acid.

$U_3O_8$ is readily soluble in nitric acid, but dissolves with difficulty in hydrochloric acid. $V_2O_5$ dissolves with difficulty in nitric acid but easily in hydrochloric (red colored solution) $U_3O_8$ is readily soluble in a mixture of glacial acetic-nitric acids (100: 5), $V_2O_5$ and $Fe_2O_3$ (ignited) are practically insoluble in this reagent.

*The salts*, $UF_4$ and $UO_2(HPO_4)_2 .4H_2O$, are insoluble in water, but dissolve in strong mineral acids.

**Solution of Ores.** — One gram or more of the ore is dissolved with 15 to 20 cc. of aqua regia, by placing the mixture first on the steam bath for ten to fifteen minutes and then gently boiling over a low flame or on the hot plate. The solution is taken to dryness, silica dehydrated as usual, the residue treated with 10 cc. of hot dilute hydrochloric acid and diluted to about 50 cc. with hot water and the silica filtered off. Uranium passes into the filtrate. The solution is now treated as directed under Separations. If much silica or acid-insoluble matter is present, this should be treated in a platinum dish with strong hydrofluoric acid, and evaporated twice on the steam bath with hydrochloric acid to expel HF. The residue, dissolved with hydrochloric acid and water, is added to the first portion of solution obtained.

**Carnotite.** — Solution of the ore is readily effected by boiling with nitric acid to which a little hydrofluoric acid is added. One gram of ore with 20 cc. nitric acid and 5 cc. hydrofluoric acid at boiling temperature will be completely decomposed in five minutes. Some authorities recommend addition of sulphuric acid with ores containing barium to break up the combination of barium and uranium. If the lead acetate separation of vanadium is used, the sulphuric acid should be expelled previously to this separation. Consult the gravimetric procedures following the section on "Separations."

## GRAVIMETRIC DETERMINATION OF URANIUM AS THE OXIDE, $U_3O_8$

The methods of analysis provide for the necessary separations. The following procedure is a standard method for determining uranium in ores. [1]

**Solution of the Sample** — Take 0.5 gram of the finely ground ore, or more, according to richness. Treat by heating gently in an 8 oz. "copper flask" with nitric or hydrochloric acid, or both, together with about 1–2 cc. of hydrofluoric acid, to effect complete solution of the uranium. Sometimes galena is present, in which case it is best to start with 10 cc. or more of hydrochloric acid and heat until the galena is decomposed. Whenever hydrochloric acid is used, boil almost to dryness to expel most of it before continuing. To this residue, or to the original ore, if hydrochloric acid appeared unnecessary, add 10 cc. of nitric acid and 1–2 cc. of hydrofluoric acid. Boil very gently to effect complete decomposition, and finally to approximate dryness. Allow to cool, add 3 cc. of nitric acid and 50 cc. of hot water, and see that everything soluble is dissolved.

### Removal of Interfering Elements

Now make slightly alkaline with ammonia, then just acid with nitric acid, and again alkaline with a little solid ammonium carbonate, followed by about 5 cc. of strong ammonia and 3–4 grams more of ammonium carbonate.

Boil for about a minute and then filter, having a wetted wad of absorbent cotton in the apex of the filter. Wash twice with hot water. Boil and concentrate the filtrate in a covered beaker during the next step.

Dissolve the precipitate on the filter with a little hot dilute nitric acid, receiving the filtrate in the original flask. Again neutralize and precipitate as before, washing this second precipitate well with hot water. Add the filtrate to the first one and continue the concentration to 150–200 cc. Now acidify with nitric acid, and then, in case of doubt, add about 1 cc. of hydrogen peroxide. A reddish brown color indicates vanadium.

A. *Vanadium Present.* — Boil to expel any remaining $CO_2$, make just alkaline with ammonia, then just acid with nitric acid, finally adding about 4 cc. of the latter in excess. The appearance of the liquid is usually a sufficient indication of the neutralization points. Now add 1 gram of lead acetate crystals and then sufficient ammonium acetate solution (about 20 cc.) to neutralize the nitric acid and precipitate the lead vanadate. Boil for about 10 minutes and then filter through a double filter, returning the first portions if not

[1] Footnote contributed by Dr. A. H. Low, Author of "Technical Methods of Ore Analysis."

perfectly clear. Wash with hot water. Receive the filtrate in a large beaker. If bulky, boil down to perhaps 200–250 cc. Now add ammonia in marked excess and boil for a minute to expel any $CO_2$. Filter hot, paying no attention to a turbid filtrate unless it is yellowish, in which case wash the precipitate once with hot water, re-acidify the filtrate with nitric acid, heat to boiling and again precipitate with ammonia, filtering through the previous precipitate. No washing is required. Place the last beaker under the funnel and fill the latter with a strong hot solution of ammonium carbonate, to which some free ammonia has been added. Usually one filling is sufficient to dissolve all the uranium and leave a white residue of lead carbonate, perhaps slightly discolored by a trace of iron. Wash with hot water, using a little more of the ammonium carbonate solution, if apparently necessary. Add to the filtrate sufficient strong hydrogen sulphide water to precipitate all the remaining lead (ordinarily 25 cc. of strong hydrogen sulphide water), or pass the gas for a short time. This also removes traces of iron. Heat to boiling, then allow to stand and settle. Filter, washing with hydrogen sulphide water containing some ammonium carbonate. Boil to expel the sulphide, then acidify with nitric acid and boil off all $CO_2$. Continue according to C.

B. *Vanadium Absent.* — Boil the nitric acid solution sufficiently to expel all $CO_2$, then add ammonia in marked excess and boil a little longer to expel any $CO_2$ in the ammonia. Filter the hot mixture, returning the first portions if not perfectly clear. No washing required. Dissolve the uranium on the filter with hot ammonium carbonate solution, as described in the last paragraph, and continue from this point as in the same situation above. Do not omit the hydrogen sulphide treatment, for, even in the absence of lead, there will usually be traces of iron to be removed. Continue according to C.

C. Add ammonia in marked excess, boil well for several minutes and then filter through an ashless filter, returning the first portions if not clear. No washing required. Ignite filter and precipitate thoroughly in a porcelain crucible and weigh, after cooling, as $U_3O_8$. Impurities are usually present.

It is always well to boil the filtrate for some time. If any more precipitate is obtained, collect it on a separate filter, ignite, weigh and add its weight to the rest.

Dissolve the residue in the crucible by warming with a little nitric acid. Dilute and test for vanadium with hydrogen peroxide. A faint brownish tinge may be neglected. Rinse the solution into a small beaker, add solid ammonium carbonate in excess, boil a minute or two and then filter through a small filter washing with hot water. The residue on the filter may consist of alumina and other insoluble matter. Ignite filter and residue in the original crucible, weigh and deduct the weight from that of the impure $U_3O_8$ previously found.

**Ammonium Acetate Solution.** — Eighty cc. of strong ammonia, 100 cc. of water and 70 cc. of 90 per cent glacial acetic acid.

Note. — A yellow filtrate from the ammonium uranate indicates incomplete precipitation. This may be due to a deficiency in ammonium nitrate, as ammonium uranate is perceptibly soluble in pure water. Add a gram or so of ammonium nitrate to the filtrate, boil and refilter. Or, better, dissolve the precipitate on the filter with dilute nitric acid, so that the mixed filtrates will be markedly acid, and repeat the precipitation with ammonia. The filtrate should be colorless.

## GLACIAL ACETIC ACID METHOD FOR DETERMINING URANIUM IN CARNOTITE[1]

The following method depends upon the fact that uranium nitrate or oxide is soluble in a mixture of glacial acetic and nitric acids in the proportion of 20 parts by volume of the former to 1 part of the latter, while vanadic nitrate and oxide ($V_2O_5$) are not.

**Procedure.** — Half a gram or more of carnotite ore according to its richness (ground to pass 100 mesh sieve), is taken for analysis and digested at boiling temperature with 25 cc. dilute $HNO_3$ (1 : 1) and 1–2 cc. HF. (An amount that will fill a small crucible lid.) The solution is rapidly evaporated to dryness and baked gently to expel water, but not ignited.

Fifteen to 20 cc. of glacial acetic-nitric reagent (20 : 1) are added, rinsing down the sides of the beaker to remove any adhering material, using a policeman if necessary. (The reagent may be conveniently handled in a small wash bottle, the transferring of precipitates and washing with the reagent being necessary, no water being used at this stage.) The residue transferred to a filter is washed with the reagent five or six times, using small portions of the mixture.

The filtrate and glacial washings are rapidly evaporated to dryness and the residue again extracted with glacial-nitric acids. This extract, free from vanadium, is evaporated to dryness, and gently heated over a free flame until the residue turns dark. Ten cc. of nitric acid and 40 cc. of water are added and the mixture heated to dissolve the uranium.

The greater part of the free nitric acid is neutralized by addition of ammonia (no permanent precipitate should form). Solid ammonium carbonate is added (covering the beaker during the intervals between additions of the carbonate as loss will occur through effervescence in an uncovered beaker) until a precipitate forms that remains undissolved on stirring. 2–3 grams of additional ammonium carbonate and 5 cc. of ammonium hydroxide are now added and the solution warmed to coagulate the hydroxides of iron and aluminum. Uranium passes into solution.

The precipitate is filtered off and washed with hot water. The filtrate and washings (concentrated by boiling to about 150 cc.–200 cc. if the volume is large) are acidified with nitric acid. (Uranium precipitates and redissolves.) Carbon dioxide is expelled by boiling and a decided excess of ammonium hydroxide added. The boiling is now continued until uranium precipitates completely. If the supernatant solution is yellow, it is again acidified with nitric acid, followed by an excess of ammonium hydroxide and the boiling repeated. This generally effects complete precipitation.

The precipitated uranium is filtered off, washing being unnecessary.

[1] Wilfred W. Scott, J. Ind. Eng. Chem., Vol. 14, No. 6, page 531. June, 1922.

The filter and precipitate are placed in a crucible, the greater part of the water expelled by drying and the material then ignited. The greenish black residue is weighed as $U_3O_8$.

This residue should be soluble when boiled with nitric acid. If it is not, contamination by iron and aluminum is indicated. Any residue remaining should be filtered off, then washed free of uranium with hot water, and ignited. Its weight is subtracted from the uranium oxide to obtain the true value of $U_3O_8$.

NOTES. — 1. C. A. Pierlé, Jour. Ind. Eng. Chem. 12, 61, 1920.

2. Uranium dissolves completely in the glacial-acetic mixture. A small amount of the vanadium may dissolve, hence the extract is evaporated and the residue again extracted. A smaller quantity of the reagent may be used in this second extraction. 25 cc. of the reagent will dissolve, at boiling temperature, about 4.5 grams of $U_3O_5$ in five minutes and about 0.003 grams of $V_2O_5$. The proportion of glacial acetic acid to nitric acid should not fall below 10: 1, otherwise vanadium will dissolve in appreciable amount. The author uses a round bottom flask filled with cold water, placing this over the beaker to act as a condenser to prevent loss of acetic acid. Very little loss occurs during the five minutes boiling.

3 The acetic acid extract filters rapidly. The red colored residue contains the vanadium and practically all of the silica, iron oxide and alumina.

4. The residue is ignited to destroy organic matter which would prevent precipitation of uranium by ammonia.

5. Uranium carbonate precipitates and then dissolves in the acid when present in excess. $CO_2$ must be expelled as this prevents precipitation of uranium by ammonium hydroxide.

6. A colored solution indicates the presence of uranium. The nitrate formed by acidification with $HNO_3$ and making alkaline with ammonia with additional boiling insured complete precipitation of uranium. This treatment is seldom necessary.

7. Nitric acid dissolves uranium oxide very easily. The oxide of iron is practically insoluble. Vanadic oxide difficultly soluble.

8. Hydrogen peroxide added to the nitric extract will produce a reddish brown color if vanadium is present.

Wash water used in transferring the uranium precipitate should contain ammonium nitrate to prevent solution of uranium.

## VOLUMETRIC DETERMINATION OF URANIUM BY REDUCTION AND OXIDATION

**Introduction.** — The determination of uranium by oxidation of the lower oxide $UO_2$ to $UO_3$ may be accomplished by means of potassium permanganate in precisely the same manner as in the determination of iron, the Jones reductor being used for the reduction of the uranic salt to the uranous form. The metal must be in solution either as a sulphate, a chloride or an acetate, but not as a nitrate. If present as a chloride the usual preventative solution of phosphoric acid and manganous sulphate solution must be present as in case of the titration of a chloride of iron, hence a sulphate solution is to be preferred.

**Procedure. Solution.** — The method for preparation of the sample, isolation of the uranium, has been given in the gravimetric method. The solution from the ammonium carbonate precipitate is acidified with sulphuric acid and boiled to expel the $CO_2$.

**Reduction.** — The uranium sulphate solution, diluted to a volume of 100 to 150 cc., containing one-sixth of its volume of sulphuric acid, is heated nearly to boiling and the organic matter that may be present oxidized by addition of just sufficient potassium permanganate solution to produce a faint pink color. Fifteen to 20 cc. of dilute sulphuric acid are passed through the 18-in. column of zinc in the Jones reductor, followed by the hot uranium sulphate solution, flowing very slowly, fifteen to twenty-five minutes being required for 0.2 gram of uranium oxide, thirty to forty minutes for 0.3 gram of the oxide, care being taken that the liquid in the reductor always covers the zinc.[1] The uranic solution is followed by 10 to 15 cc. of dilute 1 : 6 solution of sulphuric acid.

**Titration.** — The olive green solution is poured into a beaker or casserole. The lower oxides are immediately oxidized to $UO_2$ by the air, as seen by the slight change of color to sea green. The hot solution is now titrated with tenth normal permanganate. The solution during titration gradually becomes more and more yellowish green, as the highest oxidation is approached, until a faint pink color is obtained. With large amounts of uranium the color appears a yellowish pink.

One cc. 0.1N./$KMnO_4$ = 0.11925 gram U.

Note. 55.85 grams Fe is equivalent to 119.25 grams U. — Sutton.

[1] Hydrogen dioxide formed by nascent hydrogen in contact with air would vitiate results. — Gooch.

## VANADIUM

**V, at.wt. 51.0; sp.gr. 6.025; m.p. 1720° C.; oxides $V_2O$, $V_2O_2$, $V_2O_3$, $V_2O_4$, $V_2O_5$; vanadates — meta $NaVO_3$, ortho $Na_3VO_4$, pyro $Na_4V_2O_7$, tetra $Na_3HV_6O_{17}$, hexa $Na_2H_2V_6O_{17}$**

The materials in which the estimation of vanadium is desired may be surmised from the following facts: Industrial application. Vanadium is used in special iron and steel alloys. It increases the strength of steel as well as the compression power, without loss of hardness, and increases the resistance to abrasion; hence vanadium steels are used in locomotive and automobile cylinders, pistons, bushings and all parts of machines subject to jar. It is used in high-speed tools, vanadium bronzes for gears, trolley wheels, etc. It is used in indelible inks, and in the form of alkali vanadates and hypovanadates it serves as a mordant for aniline black on silk, for calico printing and like uses. Vanadium salts are used in ceramics where a golden glaze is desired.

### OCCURRENCE

The element occurs widely distributed in minute quantities. It is found in ores, hence occurs in blast-furnace slags as the oxide, $V_2O_5$. The principal minerals of vanadium are:

**Minerals.** — *Patronite,* a sulphide of vanadium, a nickel bearing pyrite containing free sulphur, containing 28–34% $V_2O_5$, associated with carbonaceous matter. Color greenish-black, resembling slaty coal. Hardness 2.5–3.5.

*Vanadinite,* $(PbCl)Pb_4(VO_4)_3$, containing 8 to 21% $V_2O_5$, a brittle, opaque or translucent, deep red, yellow or brown mineral with resinous lustre, giving a white to pale yellow streak; hardness 3. It consists of small sharp, hexagonal prisms, also globular masses of crystals.

*Roscoelite,* a vanadium mica with variable composition, dark green to brown in color, with minute scales having a micaceous cleavage. Hardness 2.

*Carnotite,* $K_2O{\cdot}2UO_2{\cdot}V_2O_5{.}3H_2O$, contains 19 to 20% $V_2O_5$.

*Vescloizite,* $(PbZn)_2NVO_5$, contains 20 to 22% $V_2O_5$.

*Eusynchite,* contains 17 to 24% $V_2O_5$.

*Cuprodescloizite,* $(PbZnCu)_2(OH)VO_4$, contains 17 to 22% $V_2O_5$.

*Calciovolborthite,* $(CuCa)_2(OH)VO_4$, contains 37 to 39% $V_2O_4$.

*Vanadium* occurs in ores of copper and lead, it is present in certain clays and basalts, in soda ash, phosphate soda, and in some hard coals.

### DETECTION

**Ammonium Sulphide or Hydrogen Sulphide** passed into an ammoniacal solution of vanadium precipitates brown $V_2S_5$, soluble in an excess of alkali sulphide and in alkalies, forming the brownish-red thio-solution, from which the sulphide may be reprecipitated by acids.

**Reducing Agents.** — Metallic zinc, sulphites ($SO_2$), oxalic acid, tartaric acid, sugar, alcohol, hydrogen sulphide, hydrochloric acid, hydrobromic and hydriodic acids (KI) reduce the acid solutions of vanadates with formation of a *blue-colored* liquid. (See Volumetric Methods.) Reduction is hastened by heating.

**Hydrogen Peroxide** added to a cold acid solution of vanadium produces a *brown color*, changing to blue upon application of heat.

**Solid Ammonium Chloride** added to a neutral or slightly alkaline solution of a vanadate precipitates the colorless, crystalline salt, $NH_4VO_3$, insoluble in ammonium chloride. The ammonium metavanadate ignited is decomposed, ammonia volatilizing and the red pentoxide of vanadium remaining as a residue.

The colorless ammonium vanadate solution becomes yellow when slightly acidified. Acids produce a red color when added to the solid salt.

*The oxide, $V_2O_5$, is distinguished from $Fe_2O_3$* by the fact that it fuses very readily with the heat of Bunsen burner, whereas the oxide of iron, $Fe_2O_3$, is infusible in the heat of a blast lamp. M.p. $V_2O_5$ = 658° C.; m.p. $Fe_2O_3$ = 1548° C.

**Comparison of Vanadium and Chromium Salts.** — Vanadium, like chromium, forms a soluble salt upon fusion with sodium carbonate and potassium nitrate or with sodium peroxide. The solution of vanadates and of chromates are yellow or orange; the color of the chromate becomes more intense when strongly acidified, whereas that of the vanadate is reduced. The yellow color of the vanadate solution is destroyed by boiling with an excess of alkali, but may be restored by neutralizing the alkali with acid. The chromate color is not destroyed. (Yellow with alkalies, orange in acid solution.) Silver nitrate produces a dark-maroon precipitate with a soluble chromate and an orange-colored precipitate with a vanadate; mercurous nitrate produces a red-colored precipitate with chromates and a yellow with vanadates. *Vanadates are also distinguished from chromates by the reduction test;* reducing agents such as a soluble sulphite, or sulphurous acid added to acid solutions, form *a blue-colored liquid with vanadates and a green color with chromates. Ammonium hydroxide* added in excess to the cold reduced solutions gives a brown color, or a brown to dirty green precipitate with *vanadium*, and violet or lavender color or a light green-colored precipitate with *chromium*, depending upon the concentration of the solutions. Hydrogen peroxide added to the reduced cold acid solutions changes the vanadium blue to reddish brown; the chromium green remains unchanged.

Reduction with zinc is rapid with vanadates, much less vigorous with

chromates. $V_2O_5$ reduced to $V_2O_2$, color changes to blue, green, lavender and finally violet. $SO_2$ or $H_2S$ reduces $V_2O_5$ to $V_2O_4$. $V_2O_2$ forms vanadyl salts.

**Detection of Vanadium in Steel.** — Five grams of the sample are dissolved in dilute nitric acid, the nitrous fumes boiled off, the solution cooled, and an excess of sodium bismuthate added. After filtering through an asbestos filter an excess of concentrated ferrous sulphate solution is added and the solution divided into two equal parts in test-tubes. To one portion 10 cc. of hydrogen peroxide are added and to the other 10 cc. of water. If vanadium is present the peroxide solution will show a deeper color than the untreated solution. A deep red color is produced with high vanadium steels and a brownish-red with low. Since titanium also causes this color, it would interfere, if it were not for the fact that the color produced with titanium is destroyed by hydrofluoric acid and fluorides, whereas that of vanadium is not. In presence of titanium, 5 cc. of hydrofluoric acid are added to the treated sample.

The brown color produced by hydrogen peroxide, with vanadium solutions, will remain in the water portion when shaken with ether. The ether layer is colored a transient blue in presence of chromium.

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

In decomposition of the material for analysis the following facts regarding the solubility of the metal, its oxides and principal salts, will be helpful:

**Element.** — The metal is not attacked by aqueous alkalies, but is soluble by fusion with potassium or sodium hydroxide and sodium carbonate containing potassium nitrate. It is insoluble in dilute hydrochloric and sulphuric acids. It dissolves in concentrated sulphuric acid and in dilute and concentrated nitric acid forming blue solutions.

**Oxides.** — $V_2O_2$, $V_2O_4$ and $V_2O_5$ are easily soluble in dilute acids, and alkali hydroxides.

$V_2O_3$ is insoluble in hydrochloric and sulphuric acids, and in alkali solutions. It dissolves in hydrofluoric acid, and in nitric acid.

**Salts.** — Ammonium meta vanadate, $NH_4VO_3$, is slightly soluble in cold water, readily soluble in hot water. The presence of ammonium chloride renders the salt less soluble. The vanadates of lead, mercury and silver are difficultly soluble in water. These are dissolved, or are transposed by mineral acids, the vanadium going into solution; i.e., lead vanadate treated with sulphuric acid precipitates lead sulphate and vanadic acid passes into solution.

### General Procedure for Decomposition

**Ores and Material High in Silica.** — The sample is treated in a platinum dish with about ten times its weight of hydrofluoric acid (10 to 50 cc.) and 2 to 5 cc. of strong sulphuric acid. The silica is expelled as $SiF_4$ and the hydrofluoric acid driven off by taking the solution to $SO_3$ fumes. The residue is extracted with hot water containing a little sulphuric acid. Any undissolved residue may be brought into solution by fusion with potassium acid sulphate, $KHSO_4$, and extraction with hot water containing $H_2SO_4$. The iron passes into solution with vanadium.

**Products Low in Silica.** — Decomposition may be effected by fusion in a nickel crucible with sodium peroxide and extraction with water. The water should be added cautiously, as the reaction is vigorous. One gram of the finely divided ore is intimately mixed with 3 to 4 grams of $Na_2O_2$ and 1 gram of the peroxide placed on the charge. The material is then fused. The iron, steel, and ores may be decomposed by fusion with $Na_2CO_3$ and $KNO_3$.

Vanadium may be determined volumetrically after removal of the hydrogen sulphide group, by titration with potassium permanganate according to the procedure given later.

**Alloys.** — These may be decomposed with nitric acid, or aqua regia.

## GRAVIMETRIC METHODS

The following procedures presuppose that vanadium is present in the solution as an alkali vanadate, the form in which it occurs in the water extract from a fusion with sodium carbonate and potassium nitrate, as is described in the method of solution of ores containing vanadium. Chromium, arsenic, phosphorus, molybdenum and tungsten, if present in the ore will be found in this solution.

### GRAVIMETRIC METHOD OF DETERMINING VANADIUM BY PRECIPITATION WITH LEAD ACETATE [1]

**Principle.** — From a weakly acetic acid solution, vanadium is quantitatively precipitated by lead acetate. The precipitate is dissolved in nitric acid, lead removed as a sulphate, and vanadium determined in the filtrate by taking to dryness and igniting to the oxide, $V_2O_5$.

**Procedure.** — To the alkaline solution or an aliquot portion obtained by extraction of the carbonate fusion of the ore with water, just sufficient amount of nitric acid is added to nearly neutralize the alkali present, as in the case of the method described for precipitation of vanadium by mercurous nitrate, and then a 10% solution of lead acetate is added in slight excess with continuous stirring. The precipitate is allowed to settle on the steam bath. The vanadate, first appearing orange colored, will fade to white upon standing. The lead vanadate is filtered and washed free of the excess of lead acetate with water containing acetic acid. The precipitate is washed into a porcelain dish with a little dilute nitric acid, and brought into solution by warming the lead salt with nitric acid. To this, the ash of the incinerated filter is added. Sufficient sulphuric acid is added to precipitate completely the lead, and the solution taken to small volume on the water bath and then to $SO_3$ fumes, but not to dryness. About 100 cc. of water are added and the mixture filtered; lead sulphate will remain upon the filter and the vanadium will be in solution. The lead sulphate is washed free of vanadium (i.e., until the washings no longer give a brown color with hydrogen peroxide).

The filtrate containing all the vanadium is evaporated to small volume in the porcelain dish, then transferred to a weighed platinum crucible and evaporated to dryness on the water bath and finally the residue ($V_2O_5$) heated to a dull redness over a Bunsen flame.

$$V_2O_5 \times 0.5604 = V$$

Notes. Lead may be separated from the vanadium by passing $H_2S$ through the nitric acid solution, the excess of $H_2S$ volatilized by boiling and the liberated sulphur filtered off. The filtrate is evaporated to dryness and the vanadium ignited with a few drops of nitric acid to the oxide $V_2O_5$.

Lead may also be separated as lead chloride in the presence of alcohol, the solution taken to dryness and vanadium oxidized by addition of nitric acid and ignited to $V_2O_5$.

Note volumetric method on page 632.

[1] Method by Roscoe, Ann. Chem. Pharm., Supplement 8, 102, 1872.

## VOLUMETRIC PROCEDURES FOR THE DETERMINATION OF VANADIUM

### POTASSIUM PERMANGANATE METHOD

#### Reduction of the Vanadate, $V_2O_5$, to Vanadyl Condition, $V_2O_4$, and Reoxidation with Potassium Permanganate

**Principle.** — Vanadium in solution as a vanadate is reduced to the vanadyl salt by $H_2S$ or $SO_2$, the excess of the reducing agent expelled and the solution titrated with standard $KMnO_4$, vanadium being oxidized to its highest form, $V_2O_5$.

**Reactions.** — *a*. $V_2O_5 + SO_2 = V_2O_4 + SO_3$. *b*. $V_2O_4 + O = V_2O_5$. Hence

$$N/10 \text{ sol.} = \frac{\text{At. wt. V}}{10} \text{ grams to the liter.}$$

**Procedure.** — An aliquot portion of the solution containing vanadium, as obtained by one of the procedures given for the solution of the sample, is taken for analysis; dilute sulphuric acid (1 : 1) is added to acid reaction and 5 cc. of acid per 100 cc. of solution added in excess. The vanadium content should be not over 0.5 gram when a tenth normal permanganate is used for the titration. *If arsenic or molybdenum is present* these may be removed from the solution by passing in $H_2S$. The insoluble sulphides are filtered off and washed with $H_2S$ water. The filtrate is boiled down to two-thirds of its volume and the sulphur filtered off. In the absence of members of the $H_2S$ group, this portion of the procedure is omitted.

**Oxidation with $KMnO_4$.** — The solution containing the vanadium is oxidized by adding, from a burette, tenth normal potassium permanganate to a faint permanent pink. If the solution has been treated with $H_2S$, the vanadium is in the vanadyl condition, and the amount of permanganate required to oxidize the solution completely will give a close approximate value for the vanadium present, each cc. of N/10 $KMnO_4$ being equivalent to 0.0051 gram of vanadium.

**Reduction.** — The vanadite is now reduced to vanadyl salt by passing through the acid solution, containing approximately 5% of free sulphuric acid, a steady stream of $SO_2$ gas. Reduction may also be accomplished by adding sodium metabisulphite, or sodium sulphite to the acid solution. The excess $SO_2$ is now removed by boiling (a current of $CO_2$ passed into the hot solution will assist in the complete expulsion of the $SO_2$).

Note. $KMnO_4$ is reduced by $SO_2$.

**Test for Iron.** — A drop test with potassium ferricyanide, $K_3Fe(CN)_6$, on a white tile will give a blue color in the presence of ferrous

iron. Since ferrous iron will titrate with potassium permanganate, its oxidation is necessary. This is accomplished by adding tenth normal potassium dichromate solution cautiously to the cold liquid until no blue color is produced by the spot test with $K_3Fe(CN)_6$ outside indicator. If the sample is sufficiently dilute, the blue color of the vanadyl solution will not interfere in getting the point where the iron is completely oxidized. Care must be taken not to pass this end-point, otherwise $V_2O_4$ will also be oxidized and the results will be low.

Note. The action of the dichromate is selective to the extent that iron is first oxidized and then $V_2O_4$. If the amount of iron present is large a separation must be effected. In case a sodium carbonate-potassium nitrate fusion has been made and vanadium has been extracted by water, iron will not be present. A special procedure for determination of vanadium in steel is given.

**Potassium Permanganate Titration.** — N/10 $KMnO_4$ is now cautiously added until a pink color, persisting for one minute, is obtained. During the titration the solution changes from a blue color to a green, then a yellow and finally a faint pink. The reaction towards the end is apt to be slow if made in a cold solution.

Notes. In absence of chromium, it is better to make the titration in a hot solution, 60 to 80° C., the end-point being improved by heat. In case an excess of permanganate has been added, the excess may be determined by a back titration with tenth normal thiosulphate. The solution may be rerun, if desired, by repeating the reduction with $SO_2$ and the titration with $K_2Cr_2O_7$ and $KMnO_4$.

One cc. N/10 of $KMnO_4$ = 0.0051 gram of V, or = 0.00912 gram of $V_2O_5$.

For solutions containing less than 0.5% vanadium a weaker permanganate reagent should be used. A fiftieth normal permanganate solution will be found to be useful for materials low in vanadium.

The author obtained excellent results by the above procedure on materials containing small amounts of iron and chromium; with amounts equal to that of vanadium present in the solution no interference was experienced. The titration with potassium permanganate is made in cold solutions if chromium is present, as the permanganate will oxidize chromium in hot solutions.

## VOLUMETRIC DETERMINATION OF VANADIUM BY REDUCTION WITH ZINC TO $V_2O_2$

The procedure proposed by Gooch and Edgar is to reduce vanadic acid, in presence of sulphuric acid, by zinc to the oxide, $V_2O_2$; oxidation of the unstable $V_2O_2$ by the air is anticipated by means of ferric chloride or sulphate, in the receiver of the Jones reductor, the highest degree of reduction being registered by the ferrous salt formed by the reaction of the reduced vanadate on the ferric salt, i.e., $V_2O_2 + 3Fe_2O_3 = 6FeO + V_2O_5$. Compounds reduced by zinc and oxidized by $KMnO_4$ must be absent or allowed for.

**Procedure.** — The Jones reductor is set up as directed in the procedure for the determination of iron by zinc reduction. The receiver attached to the tube containing the column of zinc is charged with a solution of ferric alum in considerable excess of that required for the oxidation of the reduced vanadium. (The amalgamated zinc is cleaned by passing through the column a dilute solution of warm sulphuric acid. The final acid washings should show no further reducing action on permanganate when the reductor is clean.)[1] Gentle suction is applied, and through the column of clean amalgamated zinc are passed in succession 100 cc. of hot water, 100 cc. of 2.5% sulphuric acid, and then the solution of vanadic acid diluted to 25 cc. in a 2.5% sulphuric acid solution, and finally 100 cc. of hot water. To the receiver is added a volume of 4 cc. of syrupy phosphoric acid to decolorize the solution. The reduced iron salt is now titrated with N/10 $KMnO_4$.

One cc. N/10 of $KMnO_4$ = 0.0017 gram of V, or = 0.00304 gram of $V_2O_5$.

[1] Corrections should be made for the action of zinc upon the reagents without the vanadic acids, this blank being deducted in the test.

## DETERMINATION OF VANADIUM IN ORES, MINE AND CRUDE MILL SAMPLES [1]

**Reagents.** *Indicator.* $K_3Fe(CN)_6$. — Make up just before using in a drop bottle which has been washed out with NaOH and then with water. Place a small crystal of the salt in the bottle and wash several times to remove the oxidized coat, pouring out the washings, then add about 30 cc. of distilled water and dissolve for use.

*Ferrous ammonium sulphate,* $FeSO_4.(NH_4)_2SO_4.H_2O$. 135 grams of the salt are dissolved in a mixture of 333 cc. of sulphuric acid and 3000 cc. of water.

Standardize the solution as follows: — Take 25 cc. of the solution and add 25 cc. $H_2SO_4$. Dilute to 400 cc. and titrate with standard $K_2Cr_2O_7$ reagent using $K_3Fe(CN)_6$ indicator according to the procedure used in the determination of iron.

*Potassium permanganate,* $KMnO_4$. 3.162 grams per liter.

*Potassium dichromate,* $K_2Cr_2O_7$. 4.903 grams per liter.

Standardize with ½ gram of iron wire. (1 cc. = 0.56 g. of Fe.)

**Procedure.** *Solution of the Sample.* — Take 2.04 grams of the ore, ground to pass through a 60 mesh screen. Fuse with (about 20 times its volume) sodium peroxide in a 25 cc. iron crucible. (If the mixture can be thoroughly cintered, it is better than a complete fusion.) Take up the mass with water in a 600 cc. beaker. Add a solution of 50 cc. of strong sulphuric acid diluted with 100 cc. of water. Then dilute to 400 cc. with water.

*Titration.* — Heat to about 80° F and add just sufficient of the permanganate reagent to make the solution pink. Titrate back with a few drops of ferrous ammonium sulphate reagent until the color of the permanganate just disappears. The solution will now appear a green or blue color. Now add the "ferrous" solution until the ferric cyanide spot test shows a faint blue color, then 2 cc. excess of the "ferrous" solution. Titrate back the excess with the standard potassium dichromate reagent until the indicator shows no color on the spot plate.

Calculate the ratio of the ferrous solution and the dichromate to a common basis. Deduct the cc. of dichromate from the cc. of "ferrous" added to the bluish green solution above and divide the result by 4. With an exact N/10 solution the result will be the per cent of vanadium in the sample. [2]

**Optional Method.** — Reduce the vanadium by adding a strong solution of ferrous sulphate drop by drop until a blue color is produced with potassium ferricyanide when a drop of the solution is added to a drop of the indicator on a spot plate. Oxidize the excess

[1] The author is indebted to Mr. Theodore Marvin, Met. Dep't. C. S. M., for details of this method.

[2] Note. If the factor weight 0.51 g. is taken, 1 cc. N/10 $KMnO_4$ will equal 1% V.

$FeSO_4$ by adding N/10 $KMnO_4$ cautiously to cold solution, until the spot test no longer gives a blue with $K_4Fe(CN)_6$ solution.[1] (No blue color should develop in 30 seconds.) Now titrate the vanadium with additional $KMnO_4$ added to hot solution until a faint pink color develops. 1 cc. N/10 $KMnO_4$ = 0.0051 g. of V.

**Lead Acetate Method.** — The solution obtained from the fusion of the ore (see Preparation of the sample) is acidified with acetic acid. Then sufficient lead acetate is added to completely precipitate the vanadium (usually 2 or 3 grams, according to the amount of vanadium in the sample), the solution is stirred, allowed to settle and the lead vanadate filtered off and treated as follows: —

Take the residue on the filter (this at first appears yellow) and dissolve in a very dilute solution of nitric acid. *The acid should be hot.* Transfer to an 800 cc. beaker.

Add about 10 cc. of concentrated sulphuric acid and evaporate to fumes of $SO_3$. All traces of nitrous oxide must be expelled. Dilute to 600 cc. with distilled water, add 25 cc. of concentrated sulphuric acid, heat and titrate with standard permanganate according to the first of the volumetric procedures.

[1] See method for Vanadium in Steel under Notes.

## SPECIAL PROCEDURES

### Volumetric Determination of Molybdenum and Vanadium in Presence of One Another

Sulphur dioxide reduces $V_2O_5$ to $V_2O_4$, but does not reduce molybdic acid provided the sample contains 1 cc. of free sulphuric acid per 50 cc. of solution and not more than 0.2 gram of molybdic acid. By means of amalgamated zinc $V_2O_5$ is reduced to $V_2O_2$ and $MoO_3$ to $Mo_2O_3$. Upon these two reactions the determination is based according to the procedure worked out by Edgar. Details of the method are given in the chapter on Molybdenum, page 397.

### Volumetric Determination of Vanadium, Arsenic or Antimony in Presence of One Another. Edgar's Method

Tartaric or oxalic acid reduces $V_2O_5$ to $V_2O_4$, but does not act upon arsenic or antimony. On the other hand $SO_2$ causes the reduction of all three. Therefore if aliquot portions of the solution are taken, one portion being treated with tartaric acid and vanadium determined by titration with iodine, and another portion reduced with $SO_2$ and again titrated with iodine, the difference between the two titrations is due to the cc. of reagent required for the oxidation of the reduced arsenic or antimony.

**Reactions.** $V_2O_4 + I_2 + H_2O = V_2O_5 + 2HI.$

$As_2O_3 + V_2O_4 + 3I_2 + 3H_2O = As_2O_5 + V_2O_5 + 6HI.$

$Sb_2O_3 + V_2O_4 + 3I_2 + 3H_2O = Sb_2O_5 + V_2O_5 + 6HI.$

**Vanadium.** — One portion is boiled with about 2 grams of tartaric or oxalic acid, until the solution turns the characteristic blue of vanadium tetroxide. After cooling, the solution is nearly neutralized with potassium bicarbonate, and an excess of standard iodine solution added. Neutralization is now completed, an excess of bicarbonate added, and after fifteen to thirty minutes the excess iodine titrated with standard arsenious acid, starch being used as an indicator. This titration measures the vanadium present.

**Arsenic or Antimony.** — A second portion of the solution is placed in a pressure flask and acidified with sulphuric acid. A strong solution of sulphurous acid is added, the flask closed and heated for an hour on the steam bath. After cooling, the flask is opened and the solution transferred to an Erlenmeyer flask and the excess of $SO_2$ removed by boiling, a current of $CO_2$ being passed through the liquid. The cooled solution is treated with bicarbonate, iodine added and the titration conducted exactly as described for determination of vanadium in the first portion. The difference between the first titration and the second is a measure of the cc. required for oxidation of arsenic or antimony.

### Determination of Vanadium in Presence of Iron. Vanadium in Steel. Chromium being Absent

Two grams of the sample, (or an amount containing approximately 0.2 g. of V) are dissolved in 50 cc. of (3 : 2) $H_2SO_4$. When the action subsides, 10 cc. of $HNO_3$ are added and the solution boiled. (Refractory products decompose with addition of HF, but this should be fumed off if used.) Permanganate is now cautiously added until a faint pink color is obtained.

The vanadium is now reduced by cautious addition of ferrous salt solution (a standard solution not necessary), until a drop of the solution mixed with a drop of potassium ferricyanide indicator (a pure crystal the size of a pin head dissolved in 100 cc. of water) on a white tile shows a blue color indicating ferrous iron.

The excess ferrous iron is now cautiously oxidized with standard permanganate reagent until no blue color results[1] in the spot test. In case of doubt regarding this end-point ferrous solution is again added until the spot test gives a blue color[1] and the oxidation with permanganate repeated. If this end-point is passed the results will be low.

Vanadium is now titrated with the standard permanganate, making note of the exact amount required to produce a permanent faint red color.[1] The solution may be titrated hot in absence of chromium.

1 cc. of N/10 $KMnO_4$ will oxidize 0.0051 gram of vanadium.

### Determination of Chromium and Vanadium in the Same Solution in Presence of Iron. Chromium and Vanadium in Steel and Ferrous Alloys

The method takes advantage of the fact that both chromium and vanadium are reduced by a ferrous salt, but only vanadium is oxidized in a cold solution by potassium permanganate.

**Reagents.** — N/10 solutions of $KMnO_4$ and $FeSO_4.(NH_4)_2SO_4$.
Very dilute solution of $K_4Fe(CN)_6$ indicator for iron.

**Procedure.** — The sample is brought into solution by means of sulphuric or nitric acid or both. For convenience in titration the amount of chromium should not exceed 0.08 gram and vanadium 0.2 gram, the quantity of sample being taken accordingly.

The solution containing iron, chromium and vanadium is cautiously oxidized by adding the standard permanganate until a faint pink color is obtained. A slight excess of standard ferrous salt is now added, the amount being sufficient to completely reduce the chromium and vanadium present and about 1 cc. excess. The solution turns green (no shade of yellow being evident) and ferrous iron

[1] The amount required to oxidize the iron is not considered. 30 seconds should be allowed for the color to develope.

is evident by the spot test with the ferricyanide indicator, placed in drops on spot plate, a blue color resulting as soon as ferrous iron is in excess. Make record of the cc. required.

To the cold solution standard potassium permanganate is now added until the excess of ferrous iron is oxidized as shown by the spot test. (No blue produced with the ferricyanide solution.) [1] Make a record of the amount required to oxidize the iron.

Now continue the titration with permanganate until a faint pink or red color is obtained indicating the complete oxidation of vanadium. The color should persist for 30 seconds. Make a record of the amount of permanganate required.

**Calculation.** — The total titration with the ferrous salt minus the back titration to oxidize the excess of ferrous iron is the amount required to reduce vanadium and chromium.

The total permanganate required to produce a pink color minus the amount required to oxidize the excess of ferrous iron gives the amount of permanganate required to oxidize vanadium. (Chromium being unaffected).

Therefore

Total cc. ferrous sol. minus total cc. of $KMnO_4$ sol. multiplied by the chromium factor 0.001733 = gram of Cr. in sample.

Total cc. of $KMnO_4$ sol. minus cc. of $KMnO_4$ required by excess of ferrous salt multiplied by the vanadium factor 0.0051 = gram of V.

Note. If the ferrous solution and permanganate solution are not exactly N/10 convert the cc. used above to exactly N/10 equivalents.

[1] Dilute ferrous solutions act slowly on the ferricyanide indicator. 30 seconds should be allowed for the color to develope.

## ZINC

**Zn, at.wt. 65.37; sp.gr. 6.48 to 7.19; m.p. 419°; b.p. 920° C.; ZnO oxide**

The determination of zinc is called for in the buying and selling of ores for smelters, refuse material, e.g., from galvanizing plants, foundries, brass mills, and blast furnaces, in manufacture of brass, white metals, and alloys in general, paints and pigments, zinc chloride for preservation purposes, and in the control work in smelting of zinc and lead ores.

### OCCURRENCE

Zinc is found in nature only in combined form, the carbonate zinc spar, smithsonite; the silicate, willemite; the sulphide zinc blende, sphalerite; and the oxide, zincite, all of commercial importance. Nearly all of these ores contain cadmium. A brief description of the more important minerals follows.

**Minerals.** — *Sphalerite*, Zinc Blende, Black-Jack, ZnS, a brittle, resinous, transparent to translucent, yellow, brown or black, rarely white, green or red mineral, with resinous lustre; white to pale brown streak; hardness 3.5–4. Occurs massive, cleavable, also compact fine grains.

*Zincite*, Red Zinc Ore, ZnO, a brittle, translucent, orange-red to deep red mineral with sub-adamantine lustre, giving an orange-colored streak; hardness 4–4.5. Lamellar or granular masses.

*Smithsonite*, Dry Bone, $ZnCO_3$, white (may be yellow, brown, green or blue), brittle, translucent to opaque mineral with vitreous to dull lustre; white streak; hardness 5. Stalactitic, also porous masses and granular. Crystals often colored by iron, copper and cadmium.

*Willemite*, Troostite, $Zn_2SiO_4$, a brittle, transparent to opaque mineral with resinous lustre, colors varying from white, yellow, green, pale red, blue and brown; streak almost white; hardness 5. Compact or granular masses, occasionally radial aggregates of slender crystals.

*Calamine*, Electric Calamine, $(ZnOH)_2SiO_3$, a brittle, opaque to transparent mineral, yellow to brown, or colorless, white, rarely blue or green crystals; vitreous to pearly lustre; white streak; hardness 4.5–5. Drusy surface or in radiated groups of crystals, forming a ridge or cockscomb, rarely small transparent crystals. Granular, stalactitic, botryoidal. A constituent of some clays.

*Franklinite*, $(Fe\ Mn\ Zn)(Fe\ Mn)_2O_4$, a black, brittle, opaque mineral with metallic or dull lustre, may be slightly magnetic; streak brown to black; hardness 6–6.5. Occurs in compact masses, rounded grains and octahedral crystals.

*Zinc* is a bluish white crystalline metal; brittle at ordinary temperatures; malleable at 110–150°; brittle at 200° C. Its hardness is between that of tin and copper. At boiling temperature the metal burns in the air with a pale greenish-blue flame, forming zinc oxide. In moist air the metal is coated with a stable carbonate which acts as a protection against further action. Zinc is used in galvanizing iron to protect it from corrosion by oxidation, in this respect acting more perfectly than tin. Zinc forms an important constituent in a number of alloys. At red heat zinc decomposes water; in powdered form, it acts slowly on cold water.

**Suggestion to the Students.** — Determine zinc by the ferrocyanide method given on page 648.

### DETECTION

**General Procedure.** — After the removal of the HCl and $H_2S$ groups, Fe, Al, and Cr may be precipitated as hydroxides, or as basic acetates. Zn is now precipitated with Co, Ni and Mn from an ammoniacal solution by $H_2S$. The precipitated sulphides are treated with cold dilute HCl, whereupon Zn and Mn dissolve as chlorides. After expelling $H_2S$ by boiling, Zn is changed to the soluble $Na_2ZnO_2$ by an excess of NaOH, which precipitates Mn as the hydroxide. From the alkaline filtrate white ZnS is precipitated by $H_2S$.

**Ferrocyanide Test.** — Bring the material into solution with hydrochloric acid or nitric acid and add bromine water. Precipitate iron, aluminum and manganese with ammonium hydroxide, filter. Make the filtrate acid with hydrochloric acid adding about 10 cc. in excess for each 100 cc. of solution, now add a solution of potassium ferrocyanide, if zinc is present a white precipitate forms. Copper interferes as it also precipitates, hence if it is present it must be removed by $H_2S$ (see section on "Separations") also "General Procedure" above.

In absence of manganese and copper the procedure may be shortened. To the solution obtained above add 2–3 grams of citric acid per 200 cc. of solution, then make ammoniacal and add ferrocyanide — a white precipitate indicates zinc.

**Blow-Pipe Test.** — The finely powdered material, when heated on charcoal in the reducing flame of a blow-pipe, gives an incrustation, yellow when hot — white when cold. On moistening with cobalt nitrate and re-igniting, the mass is greenish-yellow. Materials containing above 5% Zn will give positive tests. With experience, less can be detected, but for smaller amounts the regular procedure as given under Titration in Acid Solution, Separating Zn as ZnS, should be followed, using samples as follows: For material containing 0.01–0.05%, 10 to 20 grams; 0.05–0.10%, 5 to 10 grams; 0.10–0.5%, 5 grams; 0.5% and up, 2 grams to 0.5 gram, depending on per cent of zinc present.

## METHODS FOR DETERMINATION OF ZINC

### Preparation and Solution of the Sample

**Solubility.** — Pure metallic zinc is not readily attacked by acids, but a trace of impurity acting as a catalyzer causes it to dissolve. The metal dissolves in alkalies, impurities assisting the reaction. Cold dilute $HNO_3$ dissolves Zn with evolution of $N_2O$ and NO. Strong $HNO_3$ has only a slight action, the nitrate being sparingly soluble in $HNO_3$. Hot conc. $H_2SO_4$ dissolves Zn with evolution of $SO_2$.

**Salts.** — All zinc salts are soluble in NaOH, KOH, and $NH_4OH$, except ZnS. $Zn_2Fe(CN)_6$ is insoluble in $NH_4OH$ and in HCl. ZnS is soluble in dilute HCl. The sulphide, basic carbonate, phosphate, arsenate, oxalate, and ferrocyanide of zinc are sparingly soluble in water.

**Ores.** — Most of the zinc ores are soluble in acids. High silicates may require the addition of hydrofluoric acid to effect decomposition. The aluminates may require fusion with acid potassium sulphate, $KHSO_4$, or with sodium-potassium carbonates.

The representative sample should be ground to pass a 100 mesh screen, or finer. If the material contains shot metal, it should be screened out and the percentage present calculated.

**Preliminary Procedure. Moisture Determination in the Pulp.** — One of the commonest causes of differences in zinc ore analysis is the failure to take moisture determinations on the pulp sample.

In order that analyses made on the same pulp at different times and in different laboratories may be compared it is absolutely necessary that all determinations be corrected to a dry basis. It is not sufficient that the sample be dried before or after having been pulped, but a sample for moisture must be weighed out at the same time as the sample for analysis, and the analytical result corrected for the per cent of moisture found at the time of weighing. This is especially true on roasted zinc ores which contain sulphates of zinc, iron and lime and which take up moisture quite rapidly under ordinary atmospheric conditions.

The usual temperature for drying should be 110° C., but on special ores, e.g., those containing sulphates, it is necessary to dry at 250° C. unless it is first shown that there is no loss of water above 110° C.

The determination is best made by weighing approximately two grams in a small glass-stoppered weighing tube and drying to constant weight, the weighing tube being closed with the glass stopper as soon as the tube is taken from the drying oven.

**General Procedure.** — The following procedure is generally applicable to zinc ores — 0.5–1.0 gram of the ore is treated with 10 cc. of strong hydrochloric acid. (If much silica is present it is generally

advisable to add about 5 cc. of water and then 10 cc. of HCl) heat gently and then add 10 cc. of strong nitric acid and boil down to about one third of its volume. Cool slightly and add 5 cc. of strong sulphuric acid and evaporate to sulphuric acid fumes. The decomposition may be carried out in a pear-shaped flask (such as Low's flask) or in a casserole, the evaporations being made over a free flame, or in a beaker on a hot plate (gas or electrically heated). The cooled mass may now be treated with 40–50 cc. of water and the soluble salts including zinc brought into solution by warming on a hot plate. Silica will remain insoluble and may be filtered off, and washed with hot water.

**Refractory Materials.** — Follow the general procedure to the washing of the insoluble matter. Ignite this residue in a large platinum crucible and treat by either of the following methods (*a*) Add 10 cc. of strong hydrochloric acid and 5 cc. hydrofluoric acid (as much as will be held in a platinum crucible lid) and evaporate to small volume, on a water bath. Add 5 cc. more of hydrochloric acid and again evaporate. The concentrate may now be diluted and the solution added to the main solution.

(*b*) Fuse the residue with sodium-potassium carbonates; follow this with the usual acid treatment, taking to dryness, adding acid and filtering off from $SiO_2$, adding the filtrate to the bulk of solution containing the zinc.

Zinc may now be isolated separating it from interfering substances — see "Separations."

For details of the general method for ores see under General Methods for Determination of Zinc.

**Material Containing Carbonaceous Matter.** — If the material under examination contains carbonaceous matter, coal, etc., it must be separated by taking to dryness with hydrochloric acid. Take up in acid and water, filter and wash, and evaporate the filtrate to dryness. Take up in nitric acid and proceed as in the regular method.

If the carbonaceous material is not removed, the manganese does not separate cleanly, due to the reducing action of carbonaceous compounds.

**Special Procedure for Material Containing Metallics.** — On account of the lack of uniformity in the case of metallic zinciferous material containing lead and iron, it is well to work on large samples. Five or ten grams of the metallics reduced to as fine a size as possible are weighed out and dissolved in nitric acid. The nitrous fumes are boiled off and the whole made up to 500 cc. or 1000 cc. Fifty or 100 cc. are now pipetted off into a 600-cc. beaker and the zinc titrated as usual. In case the metallic portion contains manganese, which is unusual, it can be separated by the regular procedure. Copper is separated as given under Copper-bearing Ores. Material containing cadmium should be analyzed by other methods, as given under Standard Procedure.

**Interfering Substances.** — The methods provide for the removal of interfering substances. Silica is removed by evaporation with hydrochloric acid or by taking to fumes with sulphuric acid. Evaporation with the latter acid gives silica that is easily filtered and washed. Cadmium, Lead, Arsenic, Antimony, Bismuth and Copper may be removed by precipitation as sulphides in solution of definite acidity in which zinc is soluble, or they may be removed by metallic aluminum as given in the methods that follow.

**Iron, Aluminum and Manganese.** — This separation may be effected by precipitation with ammonia and bromine, providing the quantities present are small. When large amounts are present the basic acetate procedure is followed, or, better, the zinc separated as sulphide in dilute sulphuric acid solution, pages 645, 646.

**Nickel and Cobalt.** — When nickel or cobalt are present, the only safe procedure is to separate the zinc as zinc sulphide in dilute sulphuric acid solution, as described under the standard method. Weiss has shown conclusively that zinc can be precipitated free from either cobalt or nickel under the conditions there outlined.

## GENERAL METHODS FOR DETERMINATION OF ZINC
## GRAVIMETRIC METHODS

### Weighing as Zinc Oxide

In this case the procedure is the same as in the volumetric method, in which zinc is separated as zinc sulphide up to the point where the zinc sulphide is filtered off and washed. It is now ignited in a weighed crucible and heated to 800-900° C. in a muffler for one hour and weighed as ZnO. Factor $ZnO \times 0.8034 = Zn$.

The precipitate of zinc sulphide may also be filtered on a Gooch crucible, and ignited as above.

### Weighing as Sulphate

The zinc sulphide is dissolved in hydrochloric acid. Sulphuric acid is added and the solution evaporated in a weighed crucible, all excess acid fumed off and the resulting zinc sulphate finally ignited at a dull red heat and weighed. $ZnSO_4 \times .405 = Zn$.

### Phosphate Method

Proceed as follows: — Remove the $H_2S$ group in the usual way. Boil off $H_2S$, oxidize the iron by addition of $HNO_3$ and boiling. Precipitate iron and aluminum with $NH_4Cl$ and $NH_4OH$, and filter off. Make filtrate faintly acid with HCl and add 2 cc. excess. Now add a 10% solution of sodium or ammonium phosphate and heat to boiling. Add ammonia until the precipitate dissolves, then make faintly acid with acetic acid and add 1 cc. in excess. Stir briskly (avoiding touching sides of the beaker with the stirrer) until the precipitate becomes crystalline. Allow to settle about 2 hrs. Filter on a Gooch crucible. Wash with hot water, ignite and weigh as $Zn_2P_2O_7$. Multiply by 0.429 = Zn.

### Electrolytic Method

The determination is best made from an alkaline electrolyte or one slightly acid with acetic acid and containing a considerable amount of sodium acetate. The alkaline electrolyte tends to give high results, due to the presence of zinc oxide or hydroxide in the deposit. The best results are obtained with a solution weakly acid with one of the weaker organic acids. The procedure for the acetate electrolyte is as follows:

The zinc is separated from other elements by precipitating with hydrogen sulphide in dilute sulphuric acid solution, as given under the standard method. The precipitate is filtered and washed, dissolved in hot hydrochloric acid, 5 cc. of 1 : 1 sulphuric acid added and the whole evaporated to fumes to expel hydrochloric acid. Cool and dilute, neutralize with sodium hydrate solution, make slightly alkaline, then acidify with acetic acid, and add about 5 grams of sodium acetate. The volume of solution should now be about 100 to 125 cc. Electrolyze with a platinum gauze electrode with 0.5 ampere at 5 volts.

The electrolytic methods, on account of the special apparatus needed, the experience and care necessary to get reliable results, and the unavoidable errors involved in their use, are less desirable than the gravimetric oxide method and *still less* desirable than the ferrocyanide method.

With a rotating electrode using 3 amperes current and 2.5 volts depositing zinc over an electrode coated with copper about 15 minutes are required for deposition. The zinc may be dissolved free from copper by a 1 : 1 HCl solution.

## VOLUMETRIC METHODS FOR THE DETERMINATION OF ZINC

The most accurate and generally used methods for the determination of zinc are the procedures in which potassium ferrocyanide is used as a reagent for the titration of this element. The principal differences of the methods are the modes of preparation of the sample for titration in the removal of interfering elements that form insoluble ferrocyanides, and in the use of internal or external indicators. The two methods given here have been selected with considerable care, on account of their accuracy and proven value. The first is the standard method of the New Jersey Zinc Company, that was originally worked out by Dr. F. G. Breyer; the second is a rapid method recommended by Dr. A. H. Low. Both methods are extensively used.

The following elements, forming ferrocyanides insoluble under the conditions of the zinc titration, interfere and should be provided for by either removal from the solution or by precipitation in a form that does not react with the standard reagent, — mercury, silver, cadmium, bismuth, copper, aluminum, iron, cobalt, nickel, manganese.

Most of the zinc ores are soluble in acids, the aluminates, however require fusion with bisulphate of potassium. In the acid solution silica is made insoluble by evaporation which prevents the formation of zinc silicate.

### FERROCYANIDE METHOD, INTERNAL INDICATOR

This method depends upon the separation of zinc from interfering elements by precipitating as ZnS, in a sulphuric acid solution, under definite conditions of acidity, the elements of the $H_2S$ group having been previously removed. The method is of almost universal application, and can be used on any class of zinciferous material. Copper and cadmium are easily separated and any zinc in the difficultly soluble state, e.g. spinels, etc., can easily be looked for. The method of decomposing (taking to fumes with sulphuric acid) tends to take into solution material that would be overlooked in the rapid decompositions effected in the usual methods. Moreover, the use of the internal indicator gives a very sharp end-point, so that this method is fully as accurate as any gravimetric method. The procedure, though not rapid, is recommended for routine work where the analyst is called upon to make occasional zinc analysis on all classes of materials.

The reaction with ferrocyanide and zinc may be represented as follows — $3ZnCl_2 + 2K_4Fe(CN)_6 = K_2Zn_3\,[Fe(CN)_6]_2 + 6KCl$.

**Special Reagents.** *Standard Potassium Ferrocyanide.* — This is made by dissolving 44 grams of $K_4Fe(CN)_6.3H_2O$ in water and di-

luting to 1000 cc. One cc. of this solution will precipitate approximately 0.01 gram of zinc. Frequently a more dilute solution is desired equivalent to 0.005 gram of zinc obtained by diluting the above solution with an equal volume of water. A more dilute solution than this is not recommended. The solutions used by the New Jersey Zinc Company are intermediate of the above strengths, e.g., 1 cc. of the reagent being equivalent to 0.0075 gram of zinc.

**Standardization.** — Dissolve about 0.35 gram of zinc in a 150 cc. beaker with 10 cc. of hydrochloric acid (sp. gr.) 1.2. To the solution obtained add 13 cc. of ammonium hydroxide (sp. gr. 0.9), then make faintly acid with hydrochloric acid and add 3 cc. excess. Now add 3 to 4 drops of ferrous sulphate indicator and titrate the zinc with the standard ferrocyanide according to the procedure given under Titration below. Divide the weight of zinc taken by the cc. of ferrocyanide required and the result is the value of 1 cc. of the reagent.

**Iron Indicator.** — One gram of ferrous sulphate, $FeSO_4 \cdot 7H_2O$, containing 0.2 gram of Fe, is dissolved and diluted to 1000 cc. One drop or 1/20 cc. contains 0.01 milligrams of Fe. 3 to 4 drops are sufficient for a test.

### Procedure

**Solution of the Sample.** — Such an amount of the finely ground (100 mesh) sample is taken as will contain approximately 0.2 to 0.5 gram of zinc, e.g., 5 grams of 10% zinc or 0.5 gram of 60% zinc. Place the sample in a tall 150 cc. beaker, moisten with water and add 10 cc. of strong hydrochloric acid. (If sulphides are present add also 5 cc. of nitric acid.) Cover the beaker with a clock-glass and boil the solution for half an hour. Wash off the glass cover and sides of the beaker into the solution any material that may have deposited during the boiling. With a glass rod break up any cake that may have formed and then add 10 cc. of 1 : 1 sulphuric acid and evaporate to strong sulphuric fumes. Allow to cool.

**Removal of Metals of the Hydrogen Sulphide Group.** — Add 40 to 50 cc. of water and then about 1 gram of aluminum (0.05″ mesh), cover the beaker and boil for about 15 minutes. The metals below aluminum in the electromotive series will be precipitated and iron will be reduced to the ferrous condition and remain in solution. Filter and wash with hot water.

**Removal of Cadmium.** — (Omit this step if the amount of cadmium is below 0.05 gram.) To the filtrate and washings add 5 cc. of 1 : 1 sulphuric acid and dilute to 100 cc. Pass in $H_2S$ gas for about 15 minutes. Now add drop by drop ammonium hydroxide until a yellow precipitate, CdS, appears, heat to near boiling (70° to 90° C.) and pass in $H_2S$ until no further precipitation occurs (10 to 15 minutes). Filter through a fine-grained filter, and wash the precipitate twice with 8 to 10% sulphuric acid and finally four or five times with hot water to recover any occluded zinc.

**Isolation of Zinc as Sulphide.** — Boil the filtrate and combined washings to expel $H_2S$. Add a few drops of methyl orange indicator and neutralize the free acid by adding a solution of potassium hydroxide cautiously until the red color changes to orange yellow, now add drop by drop a solution of potassium carbonate until a yellow color is obtained. To this neutral solution add 2 to 4 cc. of 5% sulphuric acid (27.2 cc. of strong $H_2SO_4$ per liter) per 100 cc. of solution. This acidity is important. (See notes.) Cool thoroughly.

Pass in $H_2S$ into this cold solution rapidly (8 bubbles or more per second) for about 40 minutes. Zinc sulphide, ZnS, precipitates in an easily filterable form (if the solution is cold). Allow to settle. Filter and wash six times with cold water.

Punch a hole through the filter and wash the precipitate into the vessel in which the precipitation was made. Now add 10 cc. of HCl to about 100 cc. of hot water and pour over the tube used in conducting $H_2S$ into the zinc solution, directing the stream over the filter and catching the acid in the beaker containing the ZnS. Boil off $H_2S$.

**Titration of the Zinc Solution.** — Add 13 cc. of ammonium hydroxide (sp. gr. 0.9), just neutralize with hydrochloric acid (litmus test) and add 3 cc. of HCl in excess, then dilute to 200 cc. Add three or four drops of ferrous sulphate indicator (0.03 to 0.04 milligrams of iron in sol.).

Heat to near boiling and pour about one-fourth of the solution into a small beaker to hold as a reserve solution. Add the standard ferrocyanide to the main solution, stirring vigorously the solution during the addition; the solution turns blue and at the end-point with a slight excess of reagent appears a creamy white. When this point is reached pour in all but 5 to 10 cc. of the reserve solution and continue the titration until the end point is again reached, add $\frac{1}{2}$ cc. excess of the reagent and wash in the remainder of the reserve solution. Continue the titration until the blue color fades to a pea green. This is the true end-point, one drop of the reagent causing the change.

Multiply the cc. required by the value of 1 cc. of the reagent in terms of zinc and the result is the amount of zinc in the sample taken.

## Notes

**Procedure with Material Containing Insoluble Zinc.** — Proceed as usual up to point where the solution is to be reduced Filter off the silica and insoluble material, wash with hot water and proceed with the filtrate as usual. Burn the insoluble residue in a platinum crucible, taking the usual precautions in case lead is present. Fume off the silica with hydrofluoric and sulphuric acids and fuse with acid potassium sulphate. Dissolve in water and sulphuric acid and proceed as in the regular method. The solution may be added to the main portion or titrated separately.

All the cadmium is separated, except about 0.05 %, which does not interfere with the titration at the given acidity.

**End-point.** — The change of color from blue to pea green is very sharp. It should be observed by looking down through the solution and not from the side. The change in color may be explained as follows: The ferrocyanide, having stood for three or four weeks, has oxidized slightly to ferricyanide, due to dissolved oxygen in the water. The few tenths of a milligram of ferrous iron added acts with this ferricyanide giving the ferro-ferricyanide blue as long as the ferrocyanide is not in excess. When it is in excess the blue is decomposed and gives the colorless ferro-ferrocyanide.

In case the ferrocyanide solution is freshly prepared, it is well to add about 300 milligrams of ferricyanide to each liter.

## Discussion on Separating Zinc as Zinc Sulphide and Titrating in Acid Solution

**Precipitation.** — The method of precipitating zinc as sulphide in sulphuric acid solution was investigated by G. Weiss (Inaugural Dissertation, Münchens 1906), and the work confirmed by F. G. Breyer. The main points of Weiss's paper are as follows:

1. Sulphate solutions are preferable to chlorides. An N/10 chloride solution is not completely precipitated by $H_2S$. Furthermore, the precipitate of sulphide from HCl solution when quantitative is not crystalline and easy to filter like that obtained from sulphate solution.

2. The concentration of a sulphate solution is without influence on the completeness of precipitation from N/10 down. That is for solutions containing at most 400 milligrams of ZnO per 100 cc.

3. Sulphate solutions of 400 milligrams of ZnO per 100 cc. may be N/100 acid with $H_2SO_4$ before beginning the precipitation. Even at acidity N/20 before precipitation less than a milligram of zinc remains unprecipitated. According to Weiss, if the solution were diluted to 300 cc., 1.3 grams of $H_2SO_4$ could be added or $6\frac{1}{2}$ cc. of 20 % $H_2SO_4$, and still have the precipitation complete. Even if as much as 10 cc. of 20 % acid were added the loss would still be only a little more than 1 milligram. Precipitating 300 milligrams from 100 cc., however, only 100 milligrams or $\frac{1}{2}$ cc. of 20 % acid could be added. This means that when the solution becomes more acid than 550 milligrams of $H_2SO_4$ per 100 cc. the precipitation of ZnS ceases. Knowing approximately the zinc content of a solution one can easily calculate the $H_2SO_4$ freed when the $ZnSO_4$ is converted into ZnS, and the difference between 550 milligrams and this calculated $H_2SO_4$ is the amount of acid that may be added when precipitating from 100 cc. of solution. For two hundred cc. of course more acid can be added, being the difference between 1,100 grams and the calculated $H_2SO_4$ freed from the $ZnSO_4$. One and one-half times the amount of Zn judged to be present is close enough for the $H_2SO_4$ freed.

4. The precipitation, under the above given conditions, is incomplete when a slow current of hydrogen sulphide is used (about four bubbles per second). One must work with as fast a stream as possible without causing mechanical losses (at least eight bubbles per second). Weiss is the first one to discuss this all-important question in the precipitation of ZnS. His explanation of the efficacy of the rapid stream of $H_2S$ is as follows:

The precipitation takes place according to the following equation:

$$ZnSO_4 + H_2S \leftrightarrows ZnS + H_2SO_4.$$

Equilibrium is reached, i.e., the velocity becomes equal in both directions, and precipitation ceases when the amount of $H_2SO_4$ per 100 cc. reaches a certain point, under a given set of conditions. Let these conditions remain exactly the same with the exception of the $H_2S$ and have the active mass of that increased. The equilibrium will be displaced from left to right and as a consequence ZnS will come down in the presence of more acid than before. $H_2S$ is not very soluble in water at room temperature, but if one increases the surface of contact between the two the $H_2S$ is dissolved much more rapidly and consequently the mass of $H_2S$ active at any time greatly increased. This is exactly what is accomplished when the zinc solution is constantly kept full of bubbles of $H_2S$. One can easily see how greatly increased the mass of $H_2S$ would be in the extreme case, when the solution is all foam.

5. A strong current of gas, like that called for above, will precipitate the usual amounts of zinc used in analytical operations in forty minutes.

6. At temperatures above 50° the precipitation is incomplete; furthermore, at room temperature the ZnS comes down in a form suitable for filtration.

Weiss found that not only were the precipitations incomplete at high temperatures, but the precipitate was finer and much more difficult to filter.

7. Water only is required for washing the precipitates.

## RAPID FERROCYANIDE METHOD FOR DETERMINING ZINC IN ORES[1]

### Outside Indicator

### Removal of Interfering Elements

1. 0.5 gram of ore. 8-oz. Erlenmeyer flask. 5 cc. of HCl, 10 cc. $HNO_3$. Boil gently almost to dryness. Remove from heat. Add 12 cc. $HNO_3$ and 5 grams (measured) of $KClO_3$. Boil gently just to dryness, finishing by manipulating flask (in holder) over free flame.

2. Add 35 cc. of Extraction Solution and heat to boiling, boiling very gently until disintegration is complete. Now add 10–25 cc. of saturated bromine water, according as manganese contents appear low or high, as indicated by brown color of residue.

3. Boil a minute or two longer and then filter through an 11 cm. filter containing a small moistened wad of absorbent cotton in the apex. Receive filtrate in a 400 cc. beaker. Wash out the flask with hot water. Remove adhering residue with rubber-tipped glass rod, or dissolve it with a few drops of HCl, then add 5 cc., or an excess, of $NH_4OH$ and rinse into filter, finally washing out flask several times with hot water. Now wash filter and residue 10 times with hot Wash Solution.

### Precipitation of $H_2S$ Group

4. Add a little litmus solution to filtrate as indicator, stir and cautiously add HCl just to acidity, then 3 cc. in excess. Dilute, if necessary, to 200–250 cc. with hot water and heat nearly to boiling. Now add 50 cc. of saturated $H_2S$ water and then the hot liquid is ready for titration.

### Titration of Zinc

5. Pour off about half the liquid as a reserve and titrate the balance until the end-point is passed. Use a spot-plate in which about 2 drops of a 15% solution of uranium nitrate have previously been placed in each depression. Transfer the zinc solution to the spot-plate with a glass tube instead of a rod, taking only a drop or two for each test, except for the final tests of the titration, when about $\frac{1}{4}$ of a cc. should be taken. After the first end-point is passed add a portion of the reserve and again pass the end-point. Repeat this, each time with more caution, until the reserve is reduced to about 5 cc. Now titrate, 6 drops at a time, until the end is again observed, then pour the entire liquid, or most of it, over the 5 cc. of the remaining reserve and then back into the same beaker again and finish

[1] Method by A. H. Low.

the titration 2 drops at a time until the end-point, or brown tinge, is plainly apparent. Read the burette. Allow a couple of minutes for the tests to fully develop and then deduct from the burette reading for as many tests as show and for 1 drop additional. Multiply the number of cc. of ferrocyanide solution used by the percentage value of 1 cc.

### Reagents

6. *Extraction Solution.* — 200 grams of commercial ammonium chloride dissolved in a mixture of 500 cc. of strong ammonia and 750 cc. of water.

*Wash Solution.* — 100 grams of commercial ammonium chloride, 50 cc. of strong ammonia. Dissolve and dilute to 1 liter.

7. *Standard Ferrocyanide.* — $K_4Fe(CN)_6$, 21.6 grams to the liter. 1 cc. = about 0.005 gram Zn, or 1%. Standardize on about 0.2 gram of pure zinc. Dissolve in 10 cc. of HCl. Dilute somewhat, neutralize as above, complete the dilution, heat and titrate precisely as described above. No filtration or $H_2S$ water necessary.

## INDUSTRIAL PRODUCTS AND RAW MATERIALS SPECIAL METHODS

### Determination of Metallic Zinc in Zinc Dust

**Discussion.** — There have been various methods proposed for determining the metallic zinc content of zinc dust. Most of these are based upon its reducing power. The latter may be determined by any one of many ways, although the results from different methods will not be concordant, due to the inaccuracies inherent with most of the methods. Potassium bichromate, iodate, ferric sulphate, and iodine have been used for measuring the reducing power of zinc dust. Fresenius also proposed dissolving the zinc dust in dilute sulphuric acid and after drying passing the hydrogen over heated copper oxide in a combustion tube, absorbing the water formed in a calcium chloride tube and weighing.

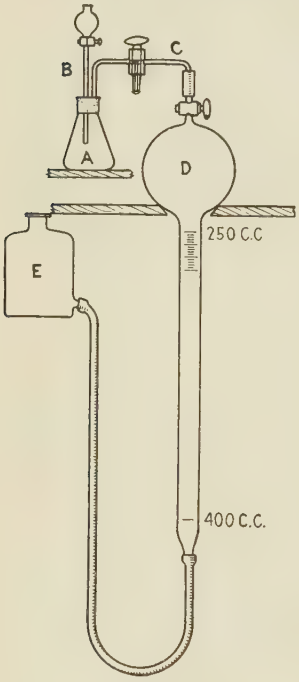


FIG. 116

There have also been methods devised based on the volume of hydrogen evolved when a sample of zinc dust is dissolved in dilute acid. Several investigators have concluded from comparative investigations that the gasometric determination of the hydrogen evolved gives the most consistently accurate results. The best arrangement of apparatus for carrying out this hydrogen evolution method is shown in Fig. 116. The time required for a determination is about 1½ hours.

**Procedure.** — One gram of zinc dust is weighed and transferred as rapidly as possible to a small Erlenmeyer flask *A*, of 100 or 200 cc. capacity, in which is placed a piece of sheet platinum about 1.5 cm. square. About 5 g. of clean unoxidized ferrous sulphate crystals are added on top of the zinc dust and the flask nearly filled with distilled water saturated at room temperature with hydrogen gas.

The object of adding the sheet platinum and ferrous sulphate is to increase the rate of hydrogen evolution by catalytic action. A further reason for adding the ferrous sulphate on top of the zinc dust sample is to coagulate the latter as much as possible when it becomes wetted, and thus prevent the floating of more than an unappreciable amount of the sample.

The rubber stopper containing separatory funnel *B* and connecting tube *C* is tightly inserted into the neck of the flask. A little distilled water is poured into *B* and the three-way stopcock in *C* turned to connect the flask with the downward outlet. Enough water is now run in from the separatory funnel to displace all the air in the flask and the connecting tube through the bore in its stopcock. The stopcock in *C* is now turned so that the downward outlet is in connection with the measuring tube *D*. By raising the leveling bottle *E*, containing 10 per cent. sulphuric acid also saturated with hydrogen at room temperature, all the gas in *D* is displaced. The stopcock in *C* is now turned through 90 deg. so as to connect the decomposing flask *A* with the measuring tube *D*. The system is hence completely filled with liquid and ready for the generation of hydrogen. The measuring tube *D* has a total capacity of 400 cc. and is graduated from 250 to 400 cc. by 0.25 cc.

Thirty cubic centimeters of 1 : 1 sulphuric acid are now poured into the separatory funnel. A small portion of this acid is allowed to run into the decomposing flask until a brisk but not too rapid evolution of hydrogen takes place. The acid, being much heavier than water, settles to the bottom of the flask and the action commences immediately. The gas evolved, together with some solution and a very small amount of zinc, passes over into the measuring tube, displacing the acid there. When the action in the decomposing flask has slowed down, more strong acid is introduced until all has been added. During this time the acid in the measuring tube and flask is shaken so as to wash down the particles of zinc dust from the upper parts of the flask and tube now filled with gas. The particles in the measuring tube on coming in contact with the 10 per cent. sulphuric acid are readily dissolved and generate their portion of hydrogen.

When all the zinc dust has been dissolved, water is run in from the separatory funnel to force the hydrogen over into the measuring tube and to fill the flask and connecting tube with water through the stopcock which is then closed. After leveling with the leveling bottle, the volume of hydrogen generated from the 1-g. sample at the prevailing atmospheric conditions is read from the measuring tube. The percentage of metallic zinc in the sample is then calculated from the following expression:

$$\text{Per cent. of Metallic Zinc} = \frac{V \times (P - p) \times 0.29196,}{(1 + 0.00367t)760,}$$

in which $V$ = volume of gas in measuring tube at atmospheric conditions, $P$ = barometric pressure, $p$ = vapor tension of water above 10 per cent. sulphuric acid at room temperature, and $t$ = room temperature.

**Necessary Precautions.** — To obtain results of the highest accuracy, it is necessary when weighing out samples of zinc dust which are very finely divided, to keep the time of exposure as small as pos-

sible in order to minimize the oxidation that takes place with the oxygen of the air. It is also highly important when samples are to

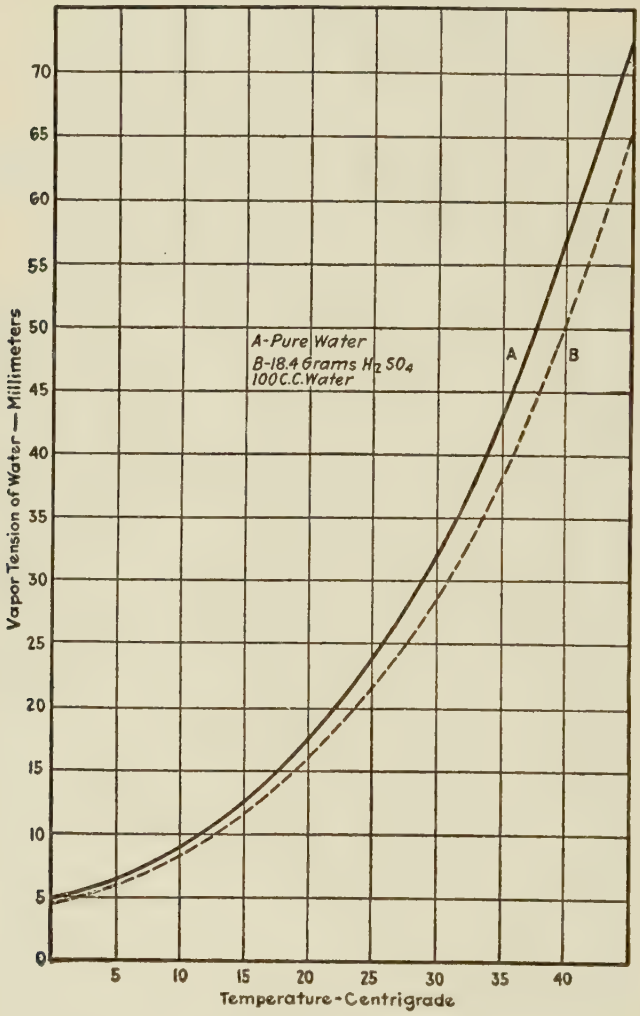



Fig. 117.

be held, that they be kept in ground glass stoppered bottles, completely filled, and sealed with paraffin or wax.

The two variables most likely to affect the results are temperature and barometric pressure. A change in the barometric pressure

is practically always extended over a reasonable length of time. A careful reading of the barometer when the volume of gas in the measuring tube is read will eliminate any error from this source. A temperature change, on the other hand, affects not only the volume of gas, according to Charles' law, but also affects the vapor tension of water and hence the actual pressure of the hydrogen when measured.

The rubber connection between the connecting and measuring tubes must be of heavy rubber and should be shellacked.

The vapor tension of water is slightly lower above 10 per cent. sulphuric acid than above pure water, as shown in Fig. 117, and for accurate work should be used in place of the ordinary vapor tension tables.

The result obtained should be corrected for any metallic impurities, as Fe, Al, etc., which evolve hydrogen when dissolved in sulphuric acid.

## DETERMINATION OF SMALL AMOUNTS OF ZINC

The following method is applicable to samples containing 0.05% Zn or less.

**Procedure.** — A large sample, 10 or 20 grams, is brought into solution by the standard procedure, taken to fumes of sulphuric acid and the zinc precipitated as sulphide after separating groups 5 and 6 by the procedures given under Standard Method, filtered and dissolved in hydrochloric acid. The sample is now washed into a 100-cc. Nessler tube, 5 cc. of ferrocyanide added and the whole made up to the mark, mixed by pouring into a beaker and then back into the tube. A standard containing the same amount of acid is made up and a standard zinc chloride solution added until the turbidity of standard and unknown are the same. From the amount of zinc added to the standard the percentage can be calculated. The standard zinc solution is made up by dissolving C.P. zinc in hydrochloric acid and diluting so that 1 cc. is equal to 1 milligram of zinc.

## ZIRCONIUM

**Zr, at.wt. 90.6; sp.gr. 4.15; m.p. 1700° ± C.; oxides $ZrO_2$, $ZrO_3$**

The determination of zirconium is required in minerals, artificial gems, incandescent gaslight mantles, firebrick, enamels, glass refractories and ferrozircon and various salts of the mineral acids. The chief source of zirconium is the mineral zircon ($ZrSiO_4$) and its valuable modifications as hyacinth. Zircon contains from 60 to 67% of $ZrO_2$.

The chief sources of Zirconium are the minerals Brazilite and Zircon. Brazilite is a hard amorphous Baddeleyite containing zircon, an unnamed zirconium silicate, iron, titanium, silica, etc., and having the empirical formula $ZrO_2$. Zircon is an ortho silicate of zirconium of the formula $ZrSiO_4$, having 60% to 67% ZrO. The precious stone "Hyacinth" is a modification of Zircon.

**Mineral.** — *Zircon*, $ZrSiO_4$, is a brittle, transparent to opaque, adamantine substance, colorless or gray, green, yellow to red or brown; streak white; hardness 7.5. Occurs generally in small, sharp cut, square prisms and pyramids, sometimes with large crystals, and in grains and lumps.

### DETECTION

The zirconium having been brought into solution by one of the methods outlined below may be distinguished:

(1) By the addition of sodium phosphate to a slightly acid solution. A white precipitate which is difficultly soluble in hydrochloric acid is characteristic of zirconium.

(2) By its solution in hydrochloric acid coloring turmeric paper orange. Titanium, however, colors it brown, and will mask the color due to zirconium; when both are present, hence it is necessary to reduce the titanium by the addition of a few pieces of zinc. Reduced titanium does not color turmeric paper, but it oxidizes rapidly, hence the test should be made as quickly as possible. Boric acid also produces a yellow color with turmeric paper, but both elements are met with in the same sample on very rare occasions only.

(3) *From Titanium* Hydrogen peroxide gives a white gelatinous precipitate of the hydrated peroxide in neutral (sulphate) solutions and ammonium carbonate gives a white precipitate soluble in large excess.

(4) *From Aluminum* by the solubility of its carbonate in an excess of alkali carbonate and also by precipitating with sodium iodate,

when a white flocculant precipitate of basic iodate is obtained from neutral solutions. The solution from ammonium carbonate if boiled precipitates the oxide, zirconia.

(5) *From Beryllium and Aluminum* Caustic alkalies give a white precipitate insoluble in excess.

(6) *From Thorium* Oxalic acid gives a precipitate soluble in excess and hydrofluoric acid does not give any precipitate.

(7) *From Glucinum* by the insolubility of its hydroxide in ammonium chloride. Glucinum hydroxide dissolves readily in the reagent.

(8) *Bead Test*[1] By fusion with sodium carbonate in the oxidizing flame a bead is obtained, which when dissolved in boiling hydrochloric acid, forms a voluminous precipitate on addition of sodium acid phosphate, if zirconium is present. *Iron, aluminum, titanium, thorium* and the *rare earths* have no influence on this test.

(9) By spectroscopic methods. Zirconium shows lines of greatest intensity in the arc spectrum at 4687.9, 4739.6, 4772.5, 4815.8, and in the spark spectrum at 3999.1, 4149.4, 4209.4, 4380.1.

[1] Biltz & Mecklenburg, Zeitscl. Angew. Chem. 1912, 25, 2110.

## METHODS OF ANALYSIS

### Preparation and Solution of the Sample

#### A. Materials Containing a Large Amount of Silica

**Decomposition by Hydrofluoric Acid.** — Five grams of the finely powdered sample are treated in a large platinum dish with 50 cc. of HF and 50 cc. of $H_2SO_4$. When the violent action has ceased the solution is evaporated first on the steam bath to expel the HF and then on a sand bath till fumes of $SO_3$ are given off. The residue is taken up with water. This usually effects complete solution of the sample. If, however, an insoluble residue still remains, it is filtered off, washed with cold water, ignited in platinum, and fused with 10 parts by weight of potassium acid sulphate. The cooled fusion is dissolved by boiling with 20% HCl. All the zirconium will now be in solution and may be determined as detailed below. Barium if present will remain insoluble and should be filtered out.

NOTES. Heating the mineral to dull redness and suddenly plunging into cold water enables zircon to be easily pulverized.

If the $KHSO_4$ fusion is extracted with dilute $H_2SO_4$ and boiled, the white basic sulphate, $3ZrO_2 \cdot SO_3$, is apt to form and remain in the residue.

#### B. General Method for Minerals, Oxides, etc.

**Decomposition by Fusion with an Alkali Carbonate.** — Two grams of the finely pulverized sample are fused with 10 grams of $Na_2CO_3$ (free of sulphur) and $\frac{1}{2}$ gram of $KNO_3$ in a large platinum dish. The melt is taken up in water and if manganese is present a few drops of alcohol are added to reduce the manganate to the manganous condition. The solution is filtered and the residue washed with dilute NaOH solution. The filtrate then contains all the silica as sodium silicate, while the residue contains all the zirconium, barium, etc. The residue is dissolved in dilute $H_2SO_4$ and the zirconium present determined as detailed below.

**C.** A convenient method for the impure oxides, which as stated above now form one of the chief sources of supply of Zirconium metal, is to reduce the ore with carbon, either with or without the addition of lime, at the temperature of the electric arc. The infusible zirconium carbide is formed, while silica, if present is reduced to the carbide also and at this temperature, being volatile is driven off. The zirconium carbide may be dissolved in warm aqua regia for analysis.

#### D. Other Methods of Decomposition Which are Sometimes Used:

Fusion with acid potassium fluoride.
Fusion with caustic soda and sodium fluoride.
By long boiling with concentrated hydrochloric acid.

## GRAVIMETRIC METHODS FOR THE DETERMINATION OF ZIRCONIUM

### Salts of Zirconium

"A" solutions containing zirconium are treated with 5 cc. of $H_2SO_4$ and evaporated to fumes; taken up with cold water and diluted to 400 cc.

"B" dry salts are treated with 5 cc. of $H_2SO_4$ and heated to fumes of $SO_3$ on a sand bath. The residue is taken up with cold water and diluted.

### Ores, Silicates, etc.

The sample having been decomposed by one of the methods outlined and the zirconium being present in solution as sulphate the liquid is diluted so as to fulfill the conditions as set forth below.

### Determination as Phosphate

To the acid solution sufficient $H_2O_2$ is added to oxidize the titanium which may be present. (The solution is colored yellow by $H_2O_2$ when titanium is present.) A sufficient quantity of ortho-phosphate, $(NH_4)_2HPO_4$ is added to precipitate all the zirconium as phosphate (aluminum and iron are not precipitated in the presence of free acid.) If titanium is present and the color bleaches after a time, more $H_2O_2$ is added until the color is restored. (Any reduced titanium is carried down with the zirconium phosphate.) The precipitate is filtered off, washed well with cold ammonium nitrate solution, ignited and weighed as zirconium phosphate, which contains 51.8% of $ZrO_2$. The solution after precipitation should be allowed to stand several hours. Traces require ten to fifteen hours, while considerable amounts of zirconium require a shorter time of settling on the steam bath for complete precipitation.

### Conditions for Accuracy

The phosphate method for determining zirconium, originally designed by W. F. Hillebrand, requires certain conditions for accurate results in estimation of large quantities of zirconium. The following details are modifications of the procedure published by Nicolardot and Reglado worked out by G. E. F. Lundell and H. B. Knowles, U. S. Bureau of Standards.

**A. Volume of Solution.** — From 25 cc. for small amounts (i.e., .0005 g. of $ZrO_2$). 200 cc. for amounts ranging around 0.1 g. $ZrO_2$.

**B. Acidity.** — Twenty per cent. $H_2SO_4$ by weight.

**C. Hydrogen Peroxide.** — Sufficient to keep $TiO_2$ peroxidized; 10 cc. will do no harm.

**D. Precipitant.** — Secondary ammonium phosphate in excess. From 10 to 100 times the theoretical requirement as expressed by the ratio $Zr : P_2C_5$, should be used. The large excess is desirable when small amounts of $ZrO_2$ are determined.

**E. Precipitation Conditions.**

1. *Temperature.* Cold or tepid, preferably 40 to 50° C.

2. *Time.* Two hours for amounts of $ZrO_2$ in excess of .005 g. Six hours or longer for smaller amounts.

**F. Filtration.** — Warm solution, decant as far as possible, to avoid clogging the filter.

**G. Washing.** — This should be done with cold 5% $NH_4NO_3$, since the phosphate is appreciably soluble in pure water.

**H. Ignition.** — Ignite very carefully in a partially covered platinum crucible over a low flame until carbon is destroyed, then blast or heat over a Meker burner for 15 minutes.

### Determination as Zirconium Oxide

With pure salts the zirconium may be precipitated completely as the hydroxide by the addition of ammonia, settling and finally igniting and weighing as the oxide, $ZrO_2$.

### Determination as Zirconium Oxide in the Presence of Iron Oxide

The aqueous solution of zirconium and iron free from other metals is treated with a slight excess of ammonia water and then boiled to remove the excess. The precipitated hydroxides are filtered off, washed with water, and dried at 105° C. The filtrate is evaporated to dryness, the residue taken up in hydrochloric acid and the solution again precipitated as before. The combined precipitates which have been dried to constant weight in a porcelain crucible are cooled and weighed as $ZrO_2 \cdot Fe_2O_3$. The oxides are then ground in a mortar, weighed into a platinum crucible and ignited to constant weight in a current of hydrogen. Only the iron is reduced to the metallic state, hence data are at hand for calculating the percentages of iron and zirconium.

# PART III

# SPECIAL SUBJECTS

## ACIDIMETRY AND ALKALIMETRY

The volumetric determination of a free acid or a free base may be accomplished with rapidity and accuracy by neutralization with a known quantity of standard base or alkali as the case may require. The point of neutralization or "end-point" is ascertained by means of certain compounds called indicators, which have a different color in acid solutions than in alkaline solutions, the point of transition from one color to the other occurs at the point of neutralization. This end point may also be recognized by the electrometric method by measuring the change of potential that occurs with the change of concentration of the hydrogen ions in the solution. This potential change is usually large and abrupt at the end point.[1]

**Indicators.** — The change of color of indicators is attributed to a rearrangement of atoms in the molecule or to the fact that in certain cases the ions have different color than the undissociated molecule.[2] In making acidimetric or alkalimetric titrations it must be remembered that the choice of indicators is important. In titrating phosphoric acid, for example, methyl orange and phenolphthalein indicate decidedly different end-points. This difference in indicators is shown in the table by Thomson[3] given on the following page.

The acid in the indicator must be weaker than the acid which it is required to determine by its means. Methyl orange, for example, is a fairly strong acid, and is not sensitive to carbonic, hydrocyanic, boric, oleic acids; on the other hand, phenolphthalein, being an extremely weak acid, is decomposed by organic acids, $H_2CO_3$, etc., hence is of value in determination of these acids.

[1] J. C. Hostetter and H. S. Roberts, J. Am. Chem. Soc., 41, 1337 (1919).

[2] Theory of indicators — Scientific Foundations of Analytical Chemistry by McGowan Waddell, J. Phys. Chem., 2, 171, 1898. Stieglitz, J. Am. Chem. Soc., 25, 1112, 1903; Am. Chem. J., 42, 115, 1909. Hewitt, Analyst, 33, 85, 1908. Noyes, J. Am. Chem. Soc., 32, 815, 1910. Thorpe Dictionary of Applied Chemistry, Vol. 1, 34–37.

[3] Volumetric Analysis, Sutton, Tenth Edition, page 44, R. T. Thomson, J.S.C., I, 12, 432.

The numerals refer in the table below to the number of atoms of hydrogen displaced by monatomic metals, such as sodium or potassium, when the indicator shows the neutral point.

| Acids | | Methyl Orange Cold | Phenolphthalein | | Litmus | |
|---|---|---|---|---|---|---|
| Name | Formula | | Cold | Hot | Cold | Hot |
| Sulphuric | $H_2SO_4$ | 2 | 2 | 2 | 2 | 2 |
| Hydrochloric | HCl | 1 | 1 | 1 | 1 | 1 |
| Nitric | $HNO_3$ | 1 | 1 | 1 | 1 | 1 |
| Thiosulphuric | ..... | 2 | 2 | 2 | 2 | 2 |
| Carbonic | $H_2CO_3$ | 0 | 1 dil. | 0 | ..... | 0 |
| Sulphurous | $H_2SO_3$ | 1 | 1 | .... | ..... | ..... |
| Hydrosulphuric | ..... | 0 | 1 dil. | 0 | ..... | 0 |
| Phosphoric | $H_3PO_4$ | 1 | 2 | .... | ..... | ..... |
| Arsenic | $H_3AsO_4$ | 1 | 2 | .... | ..... | ..... |
| Arsenious | $H_3AsO_3$ | 0 | .... | .... | 0 | 0 |
| Nitrous | $HNO_2$ | indicator destroyed | 1 | .... | 1 | ..... |
| Silicic | $H_4SiO_4$ | 0 | .... | .... | 0 | 0 |
| Boric | $H_3BO_3$ | 0 | .... | .... | ..... | ..... |
| Chromic | $H_2CrO_4$ | 1 | 2 | 2 | ..... | ..... |
| Oxalic | $H_2C_2O_4$ | ..... | 2 | 2 | 2 | 2 |
| Acetic | $HC_2H_3O_2$ | ..... | 1 | .... | 1 nearly | ..... |
| Butyric | $HC_4H_7O_2$ | ..... | 1 | .... | 1 nearly | ..... |
| Succinic | $H_2C_4H_4O_4$ | ..... | 2 | .... | 2 | ..... |
| Lactic | $HC_3H_5O_3$ | ..... | 1 | .... | 1 | ..... |
| Tartaric | $H_2C_4H_4O_6$ | ..... | 2 | .... | 2 | ..... |
| Citric | $H_3C_6H_5O_7$ | ..... | 3 | .... | ..... | ..... |

There are two general classes of indicators; (*a*) Those highly sensitive to weak acids. In this class we have phenolphthalein, turmeric, rosalic acid. (*b*) Those insensitive to very weak acids, such as carbonic, hydrosulphuric, boric acids. Among this list are methyl orange, methyl red, lacmoid, cochineal, iodeosine. These indicators are specially sensitive to bases.

Methyl orange, methyl red, phenolphthalein, lacmoid and litmus are the most commonly used indicators for acidimetry and alkalimetry. The following table shows the best conditions for the use of each:

| Indicator | Condition of Solution | General Use in Titration |
|---|---|---|
| **Methyl orange.** acids = red alkalies = yellow. | Cold solution only. | Hydrates, carbonates, bicarbonates, sulphides, arsenites, silicates, borates of sodium, potassium, ammonium, calcium, magnesium, barium, etc. |
| **Methyl red.** As above. | Cold solution only. | Especially adapted for titration of weak bases such as $NH_4OH$. |
| **Phenolphthalein.** acids = colorless alkalies = red. | Cold solutions. | Alkaline hydrates, the mineral acids, organic acids, e.g., oxalic, citric, tartaric, acetic. The indicator very sensitive to acids and adapted to titration of weak acid — carbonic acid, etc. |
| | Hot solutions. | The indicator is sensitive in hot solutions to the above. It is generally used in hot solutions for titration of acids combined with comparatively weak bases. |
| **Litmus.** acids = red alkalies = blue. | Cold solutions. | Hydrates of Na, K, $NH_3$, Ca, Ba, etc. Silicates and arsenates of Na and K, $HNO_3$, $H_2SO_4$, HCl and $H_2C_2O_4$. |
| | Hot solutions. | In addition to the above neutral and acid carbonates of K, Na, Mg; the sulphides and silicates of Na, K. |
| **Lacmoid.** In alcohol acids = red alkalies = blue. | Cold solutions. | The alkaline and alkaline earth hydrates, the arsenates, borates, mineral acids, many salts of metals which are acid to litmus and neutral to lacmoid, e.g., sulphates and chlorides of iron, copper and zinc, hence of value in determining free acids in their presence. |
| | Hot solutions. | In addition to the above, carbonates and bicarbonates of K, Na, Ca, Sr, Ba, etc. |

In general, methyl orange, methyl red and lacmoid are especially sensitive to bases, but not so sensitive to acids and are not used for weak acids. Phenolphthalein is especially sensitive to acids and is of value in titrating weak acids. Litmus is commonly used as a test indicator (litmus paper) though with careful preparation, it is valuable for general acid and alkali titration.

## ULTIMATE STANDARDS

Sulphuric and hydrochloric acids are generally used as the ultimate standard acids. Benzoic acid and other acids are also used.

Sodium carbonate is the best of the alkali standards. This salt may be prepared in exceedingly pure form. It is generally used as the basic material for the volumetric standardization of the standard acid.

### Preparation of Pure Sodium Carbonate

**Bicarbonate of Soda** made by the Ammonia-Soda process may be obtained in exceedingly pure form. The impurities that may be present are silica, ammonia, lime, arsenic, sodium chloride and sodium sulphate. With the exception of silica and lime the impurities may be readily removed by washing the bicarbonate of soda several times with cold water and decanting off the supernatant solution of each washing from the difficultly soluble bicarbonate. The washing is continued until the material is free from chlorine, as sodium chloride is the principal impurity, and its removal leaves an exceedingly pure product. The bicarbonate is dried between large filter papers in the hot air oven (100° C.).

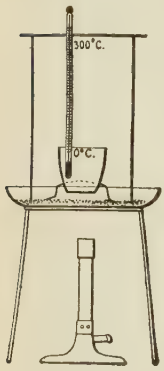


Fig. 118.

**Standard Sodium Carbonate** is made from this pure sodium bicarbonate by heating at 290° C. to 300° C. in an electric oven. If a constant-temperature oven is not available a simple oven may be improvised by use of a sand bath and a large beaker or a sheet-iron cylinder covered at the upper end as shown in Fig. 118. A thermometer passing through this shield registers the temperature of the material, within a large platinum crucible. This crucible rests upon a triangle, so that the bicarbonate is entirely surrounded by an atmosphere of comparatively even temperature.

The sodium bicarbonate is converted to the carbonate. Constant weight will be obtained in about five or six hours. When the material no longer loses weight it is cooled in a desiccator and bottled for use, preferably in several small, glass-stoppered bottles. For exceedingly accurate work the material is analyzed and allowance made for the impurities that may still remain. The error caused by any such impurities is so small that for all practical purposes it may be neglected.

This purified sodium carbonate is the ultimate standard for acidimetric and alkalimetric volumetric analysis.

Note. — F. Sutton [1] states that sodium oxalate, prepared as recommended by Sörensen, is a reliable and accurate standard for acidimetry. It is converted into sodium carbonate by moderate ignition.

Sörensen. Analyst, **28,** 307. Also 1903, 306.

C. L. Higgins, J. S. C., I. 1900, **19,** 958.

[1] Volumetric Analysis.

## PREPARATION OF STANDARD ACID

### Standard Sulphuric Acid

Fifty-two per cent sulphuric acid is in equilibrium with the average moisture present in the air of the laboratory; acid of this concentration is recommended for the standard stock solution.[1]

Pure 94 to 97% $H_2SO_4$ is diluted with sufficient water so that its gravity is about 1.4200 (42.7° Bé.). The acid is well mixed and poured into small clean and dry-stoppered sample bottles of about 200 cc. capacity. The bottles are carefully sealed and placed aside for use as desired. To determine the exact strength of this standard acid a portion is standardized against the sodium carbonate, prepared according to directions given.

**Method of Standardization. Procedure.** — A catch weight of about 10 grams of the acid is weighed out in a weighing bottle or 100-cc. beaker (10 cc. = approximately 13 grams) and placed aside for titration.[2] The amount of sulphuric acid in the sample (weight of sample multiplied by per cent divided by 100) is neutralized by 1.0808 times its weight of sodium carbonate. As an excess of acid is necessary to drive out all the carbonic acid the following formula is used: (grams $H_2SO_4$–0.05) × 1.0808 = weight of $Na_2CO_3$ required.

The required amount of sodium carbonate is weighed and transferred to a 600 cc. Erlenmeyer flask and 100 cc. of water added. The acid is carefully poured into the flask and the rinsings of the weighing bottle or beaker added. The solution is boiled for 15 minutes to expel $CO_2$. A small filtering funnel inserted in the neck of the flask prevents loss during the boiling of the acid and carbonate mixture. The excess of acid is titrated with N/5 NaOH, using phenolphthalein indicator, the caustic being added drop by drop until a faint permanent pink color is obtained.

(The sulphuric equivalent to the NaOH added) + (weight of $Na_2CO_3$ × 0.9252) = weight of pure $H_2SO_4$ present in the sample.

Notes. — $CO_2$-free water should be taken in all titrations with phenolphthalein. The indicator contains 1 gram of the compound per liter of 95% alcohol. One cc. of indicator of this strength is required for each titration.

[1] Ninety-three thousand pounds of sulphuric acid, with an exposed surface of 1260 sq. ft. and depth of 10 in., had decreased in strength from 86 per cent to 52.12 per cent $H_2SO_4$, after standing in a lead pan, protected from the rain, for 42 days (Sept. 9th to Oct. 21st, 1916). Air was bubbled through a two-liter sample of this acid for seven consecutive days, when the solution was tested and found to contain 52.18 per cent $H_2SO_4$. The average temperature of the laboratory was 74° F., the average vapor of the air (7 tests) was 0.2223 gram of $H_2O$ per standard cubic foot. The average humidity for September and October was 68 per cent; the average temperature 62° F. The average humidity for the past 33 years was 72 per cent; average temperature 57° F.

[2] See also Introduction § 6, pages 5–6.

Results should agree to within 0.05%.

The temperature of the acid should be observed at the time of standardization and this noted with results on the bottles containing the standard samples. The coefficient of expansion is .00016 + per degree F. risen in temperature or .000293 per degree C. per cc. of solution.

**Normal Sulphuric acid** contains 49.043 grams of $H_2SO_4$ per liter of solution. To make a liter of the normal acid the amount of the standard acid required is calculated by the formula

$$\frac{100 \times 49.043}{\text{per cent of } H_2SO_4 \text{ in standard}} = \text{grams of standard acid necessary.}$$

The acid is weighed out in a small beaker, a slight excess being taken (0.1 gram). The acid is washed into a liter flask and made to volume. An aliquot portion is standardized against the standard sodium carbonate. The solution may now be adjusted to the exact strength required.

**Example.** — If 25 cc. of the acid is found to contain 1.25 grams of $H_2SO_4$ we find the amount of dilution required as follows: 25 cc. of N/1 $H_2SO_4$ should contain 1.226075 grams, therefore

$$1.226075 : 25 :: 1.25 : x, \text{ and } x = \frac{25 \times 1.25}{1.226075}.$$

Then $x$ minus 25 = the amount of water required for 25 cc. Total dilution = dilution for 25 multiplied by the volume of acid remaining in the flask divided by 25 = cc. water required to make a normal acid solution.

**Fifth normal and tenth normal acids** may be prepared by diluting the normal acid to give five or ten volumes as the case requires.

**Gravimetric Methods. Precipitation as $BaSO_4$.** — Sulphuric acid may be standardized by precipitating as $BaSO_4$ according to the procedure given for sulphur. $BaSO_4 \times 0.4202 = H_2SO_4$.

**Determination as $(NH_4)_2SO_4$.** — To 10 cc. of the acid diluted to 50 cc. in a large platinum dish is added $NH_4OH$ until the acid is neutralized and a faint odor of ammonia is perceptible. The solution is evaporated to dryness on the water bath and dried at 100° C. for half an hour. The residue is weighed as $(NH_4)_2SO_4$. $(NH_4)_2SO_4 \times 0.7422$ = gram of $H_2SO_4$.

### Standard Hydrochloric Acid

This acid is occasionally preferred by chemists to sulphuric acid as a standard. At the constant boiling-point, with pressure of 760 mm., hydrochloric acid has a definite composition of 20.242% HCl. For every 10 mm. increase in pressure the percentage drops .024% and for every 10 mm. decrease in pressure the percentage rises .024%

HCl. Advantage is taken of this fact in the preparation of standard hydrochloric acid. Strong, pure HCl is distilled, the first 25 or 30 cc. being rejected. The distillate is bottled in 200cc. glass-stoppered bottles and sealed, a portion being reserved for standardization. The acid is best standardized against sodium carbonate, using the formula, Weight of HCl (weighed for analysis minus 0.05) $\times$ 1.4533 = $Na_2CO_3$ required. As in case of $H_2SO_4$ the $Na_2CO_3$ is weighed out, placed in an Erlenmeyer flask with the acid and boiled to expel $CO_2$. The excess of HCl is titrated with standard caustic. N/5 NaOH = 0.0072836 gram of HCl per cc.

The exact weight of $Na_2CO_3 \times 0.6881$ = HCl. To this add HCl obtained by NaOH titration = total HCl in the sample taken.

The exact amount of HCl being known, normal acid containing 36.468 grams HCl per liter may be made, and by diluting further, fifth normal and tenth normal acids obtained.

**Gravimetric Determination of Hydrochloric Acid by Precipitation as AgCl.** — Hydrochloric acid may be standardized by precipitation with silver nitrate solution by the procedure for determination of chlorine. AgCl $\times$ 0.2544 = HCl. It is advisable to heat the sample, diluted to a convenient volume, and add the hot silver nitrate in slight excess of that required by HCl, the amount of the reagent being calculated, e.g., mol. wt. of HCl : mol. wt. of $AgNO_3$ :: Wt. of HCl in sample : $x$.

### Benzoic Acid Standard

Benzoic acid may be obtained in exceedingly pure form by melting the resublimed acid in a covered platinum dish in a constant-temperature oven, at a temperature of 140° C. The acid is poured into test-tubes, cooled and the sticks bottled for use. The acid does not take up moisture to any appreciable extent, even when exposed to the air for some time, so that it may be weighed without danger of absorption of moisture.

### Standard Caustic Solution

Standard normal sodium hydroxide is made by dissolving approximately 50 grams of NaOH sticks with 1 to 2 grams of $Ba(OH)_2$ in 200 to 300 cc. of water and diluting to 1000 cc. The caustic is standardized against normal $H_2SO_4$, using phenolphthalein indicator. The solution is adjusted to the exact strength desired by addition of distilled water.

Note. — The addition of $Ba(OH)_2$ is made to precipitate the carbonate in the caustic, as this would interfere with titrations in presence of phenolphthalein. As the presence of barium would produce a cloudiness with $H_2SO_4$ it is advisable to add only an amount sufficient to precipitate the carbonate.

## STANDARD BURETTES

Burettes used for this work should be carefully checked for accuracy of delivery.

For accurate titration of acids or alkalies it is advisable to have a titration of 75 to 100 cc. Since the straight 100 cc. burette if gradu-

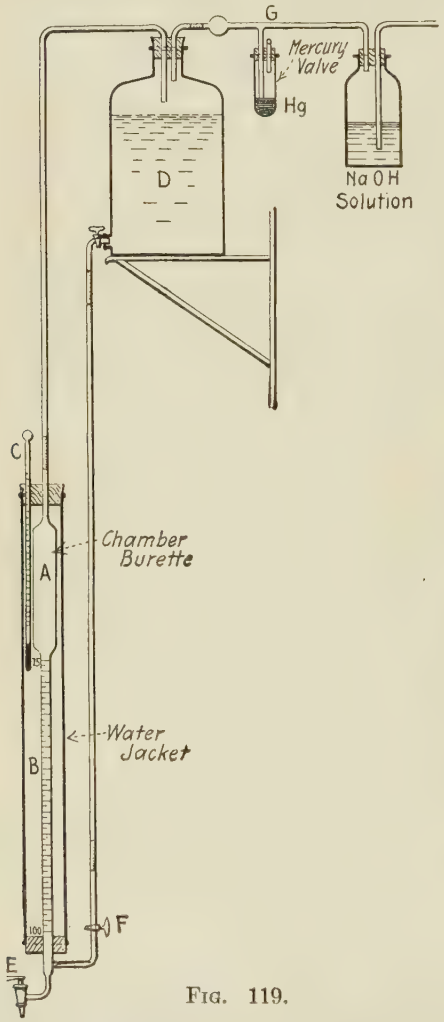



FIG. 119.

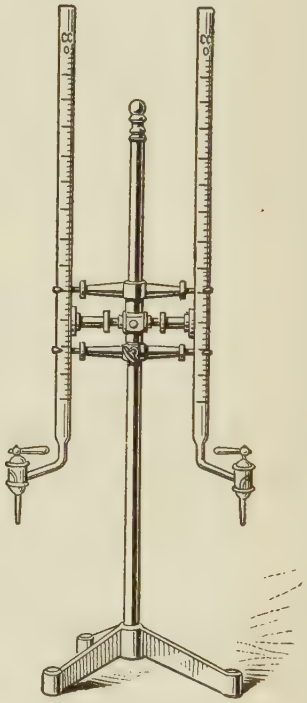


FIG. 120.
Burettes with Stand.

ated to twentieths of a cc. would be too long for convenient handling, the chamber burette is used. The chamber located in the upper

portion of the apparatus holds 75 cc., the lower portion drawn out into a uniform-bore tube is graduated in twentieths of a cc. Each tenth of a cc. has a mark passing entirely around the tube so that there will be no error in reading, the eye being held so that the mark appears to be a straight line drawn across the tube. The burette is enclosed in a large tube filled with distilled water and carrying a thermometer. The burette is connected, by means of an arm at the base, with a reservoir of standard acid. The cut, Fig. 119, shows the apparatus connected ready for use.

For class work the 50 cc. burette shown in Fig. 120 is convenient.

If vapor is lost from the standard reagents and this replaced by dry air, as in the common practice, the solution gradually changes in strength. A simple device is shown at the top of Fig. 115, which overcomes this difficulty. The air drawn into the reagent bottle is purified and saturated with moisture by passing it through sodium hydroxide. A mercury valve relieves the pressure if expansion of air in the reagent bottle occurs due to rise of temperature.

### Titration of Acids and Alkalies

In the acid titration the sample is conveniently titrated in a white porcelain casserole. This gives a white background that enables the analyst to see the end-point. The caustic is run into the acid, to within a few cc. of the end-point, rapidly and then cautiously to a faint change of color — faint pink with phenolphthalein or an orange-yellow with methyl orange. Phenolphthalein is generally preferred for acid titrations. $CO_2$-free caustic and water should always be used.

# ACIDS

## METHODS OF WEIGHING ACIDS

### Dilute Acids Non-Volatile under Ordinary Conditions

Dilute acids may be weighed directly in a beaker, weighing bottle or ordinary pipette (see directions given later) by measuring out the approximate amount desired. Since a burette reading from 75 cc. to 100 cc. should be used for this work it will be necessary to take such an amount of the acid as will require a titration between these extremes. This may be accomplished by taking the specific gravity of the acid and referring to the table for the approximate strength. From this the volume necessary may readily be calculated.

**Example.** — The case will be taken where a 75 cc. to 100 cc. burette is being used and the titration is to be made with normal caustic solution, the acid titrated being sulphuric acid. The capacity of the burette is $75 \times 0.049 = 3.675$ grams of $H_2SO_4$ to $100 \times 0.049 = 4.9$ grams of $H_2SO$. (For HCl the capacity would be 2.74 to 3.65 grams of HCl and for $HNO_3$ it would be 4.73 to 6.3 grams of $HNO_3$.)

Suppose the sulphuric acid has a sp.gr. of 1.1600. From the table for $H_2SO_4$ we find that this acid is 22.25% $H_2SO_4$, then 1 cc. contains $1.16 \times 22.25$ divided by 100 = 0.2581 gram $H_2SO_4$. Since the capacity of the burette is 3.675 to 4.9 grams $H_2SO_4$, we must weigh between $\frac{3.675}{.2225}$ to $\frac{4.9}{.2225}$ grams of the acid; to get this we should take $\frac{3.675}{.2581}$ to $\frac{4.9}{.2581}$ cc., that is to say, 14.5 to 18.5 cc. of the acid, which will weigh 16.8 grams to 21.5 grams.

### Weighing Strong Acids, Fuming or Volatile under Ordinary Conditions

The acid must be confined during weighing and until it is mixed with water or standard caustic. The best forms of apparatus include the following: —

**Lunge-Ray Pipette.** — The pipette is shown in Fig. 121. Two glass stop-cocks confine the acid in a bulb. The lower part of the pipette is protected by a ground-on test-tube. The dry pipette is weighed. Cock 2 is closed and 1 opened and a vacuum produced

in the bulb by applying suction at the upper end of pipette and closing stop-cock 1 with suction still on. The sample may now be drawn into the pipette by immersing the lower end in the sample and opening the stop-cock 2, the vacuum producing the suction. The increased weight = acid drawn in. The pipette is emptied by running the acid under water.

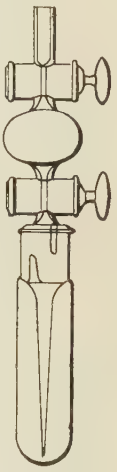


Fig. 121. Lunge-Ray Pipette.

**Dely Weighing Tube.** — This form of weighing tube has proven to be of exceptional value, to the busy works-chemist, in the analysis of oleum and mixed acids. Both speed and accuracy are gained by its use. The apparatus, shown in the cut below, consists of a long glass tube of small bore, wound in a spiral coil. Fig. 122.

The sample of acid is drawn into the weighed coil by applying suction through a rubber tube attached to *A* and drawing in the required amount of acid, a mark, ascertained by a previous run being made, indicating the point to which the acid is drawn. The tip *B* is carefully wiped off with tissue paper and the tube and sample weighed. The weight of the tube deducted gives the weight of the sample.

The apparatus is now inclined so that the acid runs back into the crook at *C* to a point marked on the wall of the tube, in order to expel as much air as possible from this end. A rubber tube filled with water is attached to *A*, the other end of the rubber tube being connected to a bottle containing distilled water. A glass bead, such as is used in rubber-tipped burettes, fitting snugly in this tube, regulates the flow of water. The Dely tube is now inverted, the tip being immersed in 150 cc. to 200 cc. of distilled water in a 4 in. casserole — Fig. 122. By pressing gently on the bead, water is slowly admitted to the tube, forcing the acid before it. The acid and water are separated by a bubble of air. Before forcing out the last half-inch of acid, the tube connected to the water supply is disconnected and the weak acid from the casserole drawn back into the Dely tube for two or three inches, then again the acid is almost entirely expelled by water from the reservoir and the procedure repeated. This is to absorb the $SO_3$ gas that invariably is present in the bubble of air above mentioned, which would be lost if forced out directly by the

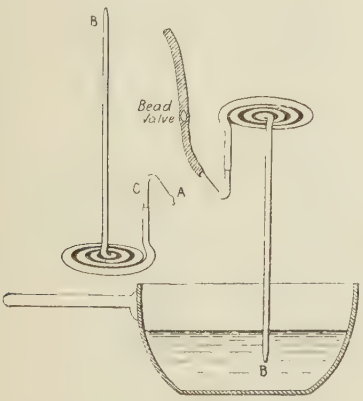



Fig. 122. Dely Weighing Tube in Operation.

water column. In order to facilitate this last step it is well to have a short rubber tube attached to the Dely tube, and a glass tip in the tube connected with the reservoir of water. The acid in the casserole, upon washing out the Dely tube, is titrated with standard caustic according to the procedure for titration of acids.

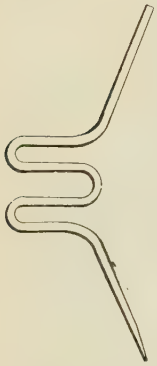


Fig. 123. Snake Tube.

The tube is dried after washing with alcohol, followed by ether, by heating on an asbestos mat on a hot plate, dry air being aspirated through.

**Snake Weighing Tube.** — The snake tube is a simple device that may be easily made by an amateur glass-blower. It is made out of a glass tube 8–10 ins. long, slightly thinner than a lead pencil. One end of the tube is drawn out to capillarity. The tube has a double bend, as shown in the illustration. It is so made that it rests on the double bend with the ends inclined upward to prevent the outflow of the acid. Fig. 123.

The tube is dried with alcohol, ether and air treatment, as in case of the Dely tube. After weighing the empty tube, acid is drawn into it by suction through an attached rubber tube. The capillary end that is dipped into the sample is wiped dry with tissue paper. The acid and tube are weighed and the acid estimated by difference.

The acid is run into 150 cc. of water in a casserole, the flow being regulated by the index finger pressed against the larger end of the tube. With careful regulation of the flow, practically no bumping occurs. With a small capillary opening it is not necessary to place the finger over the larger end of the tube as the acid flow will be slow. The tube should be kept in motion to prevent bumping from overheating any one portion. Kicking back of the acid indicates that the capillary end of the tube is too large. When the contents of the tube have run out, the tube is rinsed by sucking up some acid from the casserole and allowing it to run out, repeating several times. Suction may be applied by means

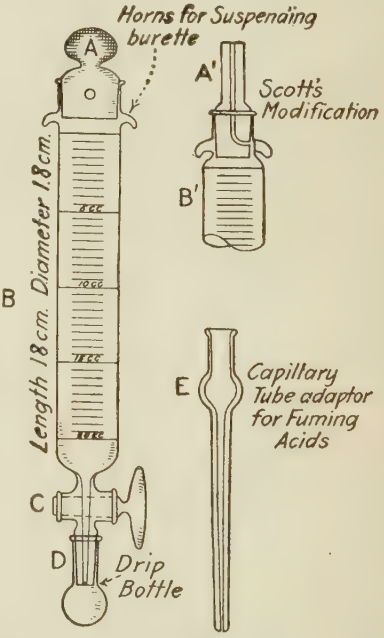



Fig. 124. Burkhard Graduated Weighing Burette.

of a rubber bulb attached to the tube. The acid is now titrated with standard caustic, using phenolphthalein indicator.

**Burkhard Graduated Weighing Burette.** — This apparatus, designed by W. E. Burkhard, is used for weighing acids or other liquids. The form for general use is shown in Fig. 124. The burette is graduated in half cc. divisions, from 0 to 20 cc. An apparatus half this size is used for oleum, where a 2 cc. sample is sufficient for a determination. For the purpose of running the sample under water a capillary tube (*E*, Fig. 124), with ground joint, is attached to the burette. This tube is placed in the solution during titration. The burette is provided with a glass vented stopper (*A*) on the top, and a glass cap for the tip, both having ground joints, to prevent escape of fumes from the sample.

W. W. Scott has modified the apparatus by replacing the fragile cap (*A*) by a tube stopper with capillary vent (see *A'*, Fig. 124). The vent to the air is opened or closed by a slight turn of this stopper. By means of this tube acid may be drawn into the burette according to the Lunge-Ray pipette procedure. With these burettes a man can control his work very accurately and save a great amount of time, both in weighing and manipulation.

In the analysis of strong oleum, about 50 grams of neutral Glauber salt are placed in a casserole containing water, and the fuming acid allowed to flow under the undissolved salt. The violent reaction of the acid with water is thus avoided. The tube *E*, Fig. 124, should be made of fused silica.

**The glass-bulb method** is still used for analysis of strong oleum. The acid weighed in a sealed tube of known weight is mixed with water by breaking the bulb in a stoppered bottle containing water, the acid is cooled and titrated as usual.

# INORGANIC ACIDS

## ANALYSIS OF MURIATIC ACID

### (Commercial Hydrochloric Acid)

### Total Acidity and Hydrochloric Acid

The usual titration with standard caustic gives the total acidity, including, in addition to hydrochloric acid, nitric and sulphuric acids which may occur in the commercial product. The acidity due to these acids is deducted from the total acidity to find the actual HCl in the muriatic acid.

A catch weight, 10 to 15 grams of the acid, is weighed in a weighing bottle, or a large snake tube, or the Dely tube, as in case of oleum analysis, and the acid allowed to mix with water in a casserole; methyl-orange indicator is added and the acid titrated with standard normal caustic solution, the red color fading to a lemon-yellow. A fraction of a drop of the alkali will cause the change when the end-point has been reached.

One cc. N/1 of NaOH = 0.03647 g. of HCl.

Note. — Hydrochloric acid may be determined gravimetrically by precipitating the chloride with silver nitrate — $HCl + AgNO_3 = AgCl + HNO_3$, or by the volumetric methods for the determination of chlorine. See Chlorine.

### Sulphuric Acid in Hydrochloric Acid

Free $H_2SO_4$. Fifty cc. of the sample is evaporated in a platinum dish (steam bath) to dryness or until the HCl has been expelled. A few drops of water are added and the material again taken to dryness (steam bath). The residue is taken up with water and titrated with N/10 of NaOH, using methyl-orange indicator. One cc. = 0.0049043 gram of $H_2SO_4$.

Multiply the $H_2SO_4$ found by 0.7436 and deduct from the total acidity above to obtain the acidity due to HCl.

### Determination of Specific Gravity

Control tests for strength of the common inorganic acids are generally made in the plant by means of the hydrometer. This instrument depends on the fact that when a solid floats in a liquid, the weight of the liquid displaced is equal to the weight of the floating body. The hydrometer is a cylindrical instrument, generally with a spherical bulb, weighted with lead shot or mercury. It has a narrow stem with graduations, which indicate the gravity. The instrument floats vertically, after displacing its own weight of solution in which it is placed. The instruments are adapted for varying gravities extending over a range of ten to twenty divisions.

By means of specific gravity tables one is able to obtain quickly and with fair degree of accuracy the strength of the acid or alkali.

Consult tables in "Standard Methods of Chemical Analysis," Scott; or D. Van Nostrand's "Chemical Annual."

The following precautions should be observed in making hydrometer tests:

1. The hydrometer should be clean and dry, and at the temperature of the liquid, before immersing to make a reading.

2. The vessel in which the observation is made should be of clear glass of suitable size and shape, to allow the hydrometer to

Fig. 125. Hydrometer.

float freely (about $\frac{2}{3}$ inch greater in diameter than the hydrometer bulb) and of sufficient height to enable full reading of the hydrometer (*i.e.*, height greater than the length of the hydrometer).

3. The liquid should be thoroughly mixed by means of a stirrer reaching to the bottom of the vessel. There should be no air bubbles in the liquid or clinging to the sides of the vessel or the hydrometer.

4. The hydrometer is slowly immersed in the liquid, slightly beyond the point where it floats and is then allowed to float freely.

5. The reading is made with the line of vision horizontal to the plane and as near as possible to this. The point is taken where this surface line cuts the hydrometer scale.

6. The temperature of the liquid is taken before and after the reading and allowance made for variation of the temperature from standard conditions as indicated in the tables.

References. — Cir. 16, 4th edition, Feb. 23, 1916, U. S. Bureau of Standards.
Sulphuric Acid Handbook by Thos. J. Sullivan, McGraw-Hill Book Co.
Thorpe's Dictionary of Applied Chemistry, pp. 103–114. Longmans, Green and Co.

## ANALYSIS OF SULPHURIC ACID

The importance of sulphuric acid to the metallurgist makes its inclusion in this work desirable. Methods for the analysis of hydrofluoric, hydrochloric and nitric acids are given in the author's work, Standard Methods of Chemical Analysis.

Sulphuric acid made by the contact process is exceedingly pure, the principal impurity being iron, which causes turbidity in strong acid. The acid made by this process is of 99% strength. This is diluted to 66° Bé (93.19% $H_2SO_4$) and is known as oil of vitriol. The acid is also commonly marketed as 60° Bé acid (77.67% $H_2SO_4$) and 50° Bé acid (62.18% $H_2SO_4$) obtained by further dilution of the stronger acid. 50° Bé acid is also obtained by the chamber process; this acid is not as pure as that produced by the contact process. The impurities occurring in sulphuric acid are iron, lead, copper, zinc, antimony, selenium, arsenic, sulphur dioxide, hydrochloric acid, hydrofluoric acid, nitric acid.

Sulphuric acid up to 93% strength may be determined with a fair degree of accuracy by ascertaining its specific gravity by means of a hydrometer and referring to the tables on sulphuric acid.

Sulphuric acid readily absorbs $SO_3$ so that its acidity may be considerably over 100%. This acid, commonly known as oleum, fumes when exposed to the air due to its low vapor tension, the $SO_3$ combining with the moisture of the air with formation of $H_2SO_4$ mist.

**Procedure for Titration with Standard NaOH.** — Concentrated sulphuric acid absorbs moisture rapidly so that the weighing should be made quickly, the acid having been placed in a special closed receptacle as recommended on page 670. Such an amount of acid is taken as will require a titration that can be read on the chamber burette used. For example if normal caustic is used and the chamber burette reads from 75 cc. to 100 cc. the acid should contain from 3.7 grams to 4.9 grams of $H_2SO_4$. The acid is added to $CO_2$-free distilled water, preferably in a porcelain casserole, 1 cc. of 1% phenolphthalein added and the titration made to a faint pink color with standard NaOH. It is advisable to titrate the acid using methyl orange if the presence of $CO_2$ is suspected in the water. Some chemists prefer the use of this indicator. It is a common practice to standardize the acidimetric and alkalimetric reagents in presence of methyl orange and phenolphthalein in separate titrations, recording factors for each.

The temperature of the titrating alkali should be noted and a correction of 0.032 cc. be made for each degree deviation from the temperature at which the reagent was standardized. For each 1° C. that the temperature is above that at standardization subtract this correction, and add this for each degree the temperature is below that at standardization.

(*cc.* titration × $H_2SO_4$ value per cc. × 100 ÷ wt. of sample = % $H_2SO_4$.)

## ALKALIES

### ANALYSIS OF SODIUM HYDROXIDE

Commercial caustic soda, purchased in blocks packed in iron drums, should be sampled with care. The hydroxide sets first on the outside, so that the impurities segregate towards the core of the block. In order to get a representative sample different sections of the block should be tapped. The material takes up moisture and carbon dioxide from the air, so that the surface of the sample should be removed before weighing. The weighing and dissolving of the sample should be done as rapidly as possible.

#### Procedure

Ten grams of the hydroxide are dissolved in water and the solution made up to exactly 500 cc. Aliquots of this solution are taken for the following determinations.

**Total Alkali.** — Fifty cc. of the caustic solution, equivalent to 1 gram of the solid, are titrated with N/1 $H_2SO_4$ in presence of methyl-orange indicator, until the faint pink end-point is obtained.

1 cc. N/1 $H_2SO_4$ = .031 grams of $Na_2O$ (total alkali actual).

NOTE. In the New York and Liverpool test N/1 $H_2SO_4$ value is .032 g. NaOH per cc.

**Sodium Hydroxide.** — Fifty cc. of the sample is treated with 100 cc. of 10% $BaCl_2$ solution and the NaOH then titrated with N/1 $H_2SO_4$ in presence of phenolphthalein.

1 cc. of N/1 $H_2SO_4$ = .04 gram of NaOH.

**Sodium Carbonate.** — Multiply the difference between the total alkali titration and the titration for NaOH by .053 and the result is grams of $Na_2CO_3$.

**Alternative Methods. Sodium Hydroxide and Sodium Carbonate.** — Carbon dioxide is readily picked up by NaOH, forming sodium carbonate, so that it is invariably present in caustic soda. The carbonate and hydrate may be determined in the same solution as follows:

Fifty cc. of the sample, equivalent to one gram of the solid, are titrated with normal $H_2SO_4$, in presence of phenolphthalein, until the pink color just disappears. This occurs when all of the sodium hydroxide is neutralized and the carbonate has been converted to bicarbonate. This titration may be recorded as cc. *A*.

Methyl orange is now added and the titration continued until the yellow color changes to pink. This titration is recorded as cc. $B$.

Then $NaOH = (A - B) \times 0.04$ and $Na_2CO_3 = 2B \times 0.053$.

### Determination of Strength of Caustic Liquors by the Hydrometer

The specific gravity of the liquor is taken by the hydrometer exactly as in case of acids. The strength of the liquor is ascertained by reference to the table on Sodium Hydroxide. See "Standard Methods of Chemical Analysis," or Van Nostrand's "Chemical Annual."

## POTASSIUM HYDROXIDE

Analysis of potassium hydroxide is similar to that of sodium hydroxide. The following molecular weights will be of use in the calculations:

$KOH = 56.11$; $K_2CO_3 = 138.21$; $KCl = 74.56$; $K_2Al_2O_4 = 196.4$; $K_2SiO_3 = 154.5$.

### Determination of Sodium Bicarbonate and Sodium Carbonate in Presence o One Another

Five grams of the sample are dissolved in $CO_2$ free water, and the solution made up to exactly 250 cc. in a measuring flask. Aliquot portions of 25 cc., equivalent to 0.5 gram, are taken for analysis. The sample taken is titrated with N/5 hydrochloric acid in presence of phenolphthalein indicator (2–3 drops). The cc. titration, recorded as "A", represents one-half of the sodium carbonate present. Methyl orange indicator is now added (2–3 drops) and the titration with the acid continued until the solution turns faintly pink. The remaining carbonate and all of the bicarbonate are now titrated. The cc. titration is recorded as B.

$$2\ A \times 0.0106 = Na_2CO_3 \text{ and } B - A \times 0.0168 = NaHCO_3.$$

The author desires to acknowledge his indebtedness to Dr. W. B. Hicks, Chief of the Analytical Department, The Solvay Process Company, for his review of the section on Alkalies.

## ANALYSIS OF AQUA AMMONIA

The per cent ammonia in a solution free from other substances may be determined with a fair degree of accuracy by determining the specific gravity of the solution by means of the hydrometer. Since the specific gravity of aqua ammonia is less than 1, hydrometers graduated for measuring liquids lighter than water are used. The formula for 1 degree Baumé = (140/sp.gr.) = 130. Reference is made to the table on Aqua Ammonia.

Provided no other basic constituent is present, free ammonia in solution is best determined by direct titration with an acid in presence of methyl orange or methyl red as indicator.

**Procedure.** — About 10 grams of the solution in a weighing bottle with glass stopper is introduced into an 800 cc. Erlenmeyer flask containing about 200 cc. of water and sufficient half normal sulphuric acid to combine with the ammonia and about 10 cc. in excess. The flask is stoppered and warmed gently. This forces out the stopper in the weighing bottle, the ammonia combining with the acid. Upon thorough mixing, the solution is cooled, and the excess of acid is titrated with half normal caustic.

One cc. $\frac{1}{2}$ N. $H_2SO_4$ = 0.0085 gram of $NH_3$.

Factor. $H_2SO_4 \times 0.3473 = NH_3$.

Note. — The aqua ammonia exposed to the air will lose ammonia, hence the sample should be kept stoppered. This loss of ammonia is quite appreciable in strong ammoniacal solutions.

## VOLUMETRIC ESTIMATION OF FREE ACID IN PRESENCE OF IRON SALTS

The red precipitate formed when solutions containing iron are titrated with caustic makes it difficult to detect the end-point of neutralization; the method suggested by C. A. Ahlum [1] takes advantage of the white compound formed by precipitating the iron as a phosphate and the fact that monosodium phosphate is neutral to methyl-orange indicator.

**Reactions:**

$Fe_2(SO_4)_3 + 2NaH_2PO_4 + x$ free acid $= 2FePO_4 + Na_2SO_4 + x$ free acid $+ 2H_2SO_4$,

or $2FeCl_3 + 2NaH_2PO_4 + x$ free acid $= 2FePO_4 + 2NaCl + x$ free acid $+ 4HCl$.

The acid equivalent to ferric iron is deducted from the total acid found, the excess acid being due to the free acid in solution.

**Procedure.** — To the solution containing the iron and free acid is added an excess of C.P. solution of monosodium phosphate (neutral to methyl-orange), and then a few drops of the indicator. The acidity of the solution is now determined by titration with standard caustic in the usual way, the solution being cold. From this titration the total free and combined acid are calculated.

Iron is now determined in a separate portion by titration with stannous chloride or dichromate.

**Calculation.**

(A) $Fe_2O_3 \times 1.2285$ = g. $H_2SO_4$ (combined). $Fe_2O_3 \times 0.9135$ = g. HCl (combined).

(B) One cc. N/5 of NaOH = .00981 gram of $H_2SO_4$ or .00729 gram of HCl.
Total acid (B) minus combined acid (A) = *free acid.*

[1] C. A. Ahlum, The Analyst, **31**, 168, 1906.

## ALLOYS

The determination of definite constituents of alloys has been considered in previous chapters. This chapter gives a general summary of the subject, dealing with the complete analysis of two typical alloys.

### Solution of Alloys and Outline of Separation

Among the solvents used may be mentioned nitric acid, aqua regia, sulphuric acid, fusion with acid fluxes.

### Nitric Acid Method

Treat one or more grams of the alloy filings or drillings with concentrated $HNO_3$ or $HNO_3$ 1 : 1 until the metal is completely decomposed or in solution, adding water if necessary to assist solution.

(*a*) *If the metal dissolves*, antimony and tin are absent; omit their tests.

(*b*) *If the metal forms a turbid solution*, antimony and tin may be present. To a portion, add several volumes of water and boil. (*a*) If a clear solution is formed treat the entire solution in the same way, and omit tests for Sn and Sb.

(*c*) If the residue is insoluble, Sb and Sn are indicated, evaporate the entire solution to dryness, gently ignite to expel water, add $HNO_3$, heat, dilute and filter. If the filtrate is turbid, repeat the filtration until clear.

**Precipitate.**—$SnO_2$; $Sn_3(PO_4)_4$; $Sb_2O_4$, all white and traces of the copper group metals.
*a.* Digest from 10 to 20 minutes with strong $K_2S$, $Na_2S$ or $(NH_4)_2S$ solution and filter.
*b.* Melt with $Na_2CO_3$ and sulphur, cool, digest with water, and filter.

**Filtrate.**—Contains the $H_2S$ group (without tin and antimony) and $(NH_4)_2S$ group.
Add from 1 to 3 cc. of concentrated $H_2SO_4$ and evaporate to fumes, cool, dilute and filter.

**Precipitate.**—Traces of copper group. If sufficient in quantity, dissolve in $HNO_3$; add to filtrate containing $(NH_4)_2S$ group.

**Filtrate.**—Contains Sn, Sb in solution. Just acidify with dilute HCl and filter.
*a.* Analyze the precipitated sulphides.
*b.* Test the filtrate for phosphates.

**Precipitate.**—$PbSO_4$, white. Treat with $NH_4C_2H_3O_2$ solution, filter, and add $K_2CrO_4$. A yellow precipitate insoluble in KOH proves lead present.

**Filtrate.**—Contains the $H_2S$ group (without Sn, Sb, and Pb and free from $HNO_3$) and the $(NH_4)_2S$ group.
Into a portion of the solution pass in $H_2S$. A precipitate shows the presence of the $H_2S$ group metals.

*a. If the $H_2S$ group is not present*, as shown by a test on a portion of the solution, make a test for the $(NH_4)_2S$ group.
*b. If the $H_2S$ group is present*, precipitate the metals with $H_2S$, filter and wash.

**Precipitate.**—Contains the $H_2S$ group, sulphides (without lead, tin and antimony).
*If mercury is present* use $(NH_4)_2S$ to separate the sub-groups.
*If mercury is absent* digest the precipitate with 20 per cent KOH (2 to 3 grams dissolved in 10 cc. of water), filter and wash.

**Precipitate.**—Copper group.
Analyze by procedure outlined for the insoluble $H_2S$ subgroup.

**Filtrate.**—Arsenic group in solution. Acidify, filter and analyze precipitate by the procedure for the soluble $H_2S$ subgroup.

**Filtrate.**—Contains the $(NH_4)_2S$ group
*a. Test for Phosphates.* If found present consult notes on this group in Part II.
*b.* Make a test for the group, by making a small portion ammoniacal, and passing in $H_2S$, if not present. A precipitate other than sulphur indicates the presence of the metals of this group. Analyze the precipitate by the first procedure on the metals of the $(NH_4)_2S$ group.
*c.* If a test is made for magnesium, analyze the filtrate by procedures for the alkalies.

## ANALYSIS OF TYPE METAL

### Alloy of Copper, Lead, Antimony, Tin, with Small Amounts of Iron and Arsenic

**Solution of the Alloy.** — To 1 gram of the alloy, which has been cut into small shavings with a clean knife, or sampled by means of a clean hack-saw producing fine "sawings," are added 15 cc. of concentrated hydrochloric acid. The solution is gently warmed on the water bath and a drop or two of concentrated nitric acid is added occasionally until solution is effected. All of the metals will be converted into chlorides which will remain in solution with the possible exception of lead chloride. An excess of nitric acid is to be avoided, as it tends to form insoluble metastannic acid, which can be readily distinguished from the crystalline lead chloride. If metastannic forms, the operation must be repeated, using less nitric acid or adding it less frequently. After a few trials the correct method of adding the nitric acid is soon acquired.

**Lead.** — The solution is allowed to cool and then stand at least one-half hour or better overnight to allow the lead chloride to crystallize out. Ten times the volume of absolute alcohol is then added in several portions. After standing for about half an hour, the lead chloride is filtered off on a Gooch crucible, washed with a mixture of 4 parts of 95% alcohol and 1 part of concentrated hydrochloric acid, and finally with pure alcohol. It is dried for three hours at 150° and weighed. The great advantage of this method of separating the lead is that the very troublesome treatment of the sulphides of the metals present with sodium or potassium sulphide is avoided. The *most difficult part* of the operation is the solution of the alloy.

**Copper and Iron.** — The filtrate from the lead chloride is heated until the alcohol is expelled. Two grams of tartaric acid and an excess of ammonia are added and the solution warmed until the precipitate dissolves. By the addition of 5 cc. of saturated hydrogen-sulphide water, the copper and the small amount of lead still unprecipitated as well as a trace of iron which may be present may be precipitated without bringing down any of the tin and antimony. The solution is warmed and when the dark-colored precipitate has settled, 1 cc. of the hydrogen-sulphide water is added to the clear supernatant liquid. If no further precipitate is produced, the solution is filtered and the precipitate washed with water containing hydrogen sulphide.

The precipitate is dissolved in a little warm dilute nitric acid and the lead separated as sulphate, the nitric acid being expelled by evaporation after the addition of sulphuric acid. The copper is precipitated from the filtrate as sulphide and if small in amount may be ignited and weighed as oxide. If considerable copper is present

it must be weighed as sulphide or without precipitation as sulphide may be separated electrolytically from the iron. One or 2 cc. of concentrated nitric acid are added and a current of one-half ampere passed until all the copper is precipitated. The iron may then be precipitated with ammonia and weighed as oxide. Copper may also be determined by the "Iodide Method" as given in the chapter on copper.

**Separation of Antimony and Tin.** — The solution of antimony and tin is acidified with hydrochloric acid, hydrogen sulphide passed, and the precipitate filtered off and washed two or three times. A hole is made in the point of the filter-paper by means of a glass rod and the bulk of the precipitate washed into a beaker with a little water. Warm dilute hydrochloric acid is poured over the paper to dissolve the portion of the precipitate still adhering to the paper. The precipitate in the beaker is dissolved by warming and adding concentrated hydrochloric acid. The hydrogen sulphide is decomposed by the addition of a crystal of potassium chlorate and warming. Some pure metallic iron is added and the solution heated on the water bath for about one-half hour or until the iron is nearly dissolved. The precipitated antimony is filtered off on a Gooch crucible, a little iron having been sprinkled on the asbestos. The precipitate is washed with boiled water to which considerable hydrochloric acid has been added. See chapter on tin for direct estimation of tin.

**The antimony** is dissolved in hydrochloric acid to which a little potassium chlorate has been added. The solution is warmed to expel chlorine and, after the addition of tartaric acid and water, hydrogen sulphide is passed. The antimony sulphide is filtered off and washed with water containing a little hydrogen sulphide. The moist precipitate is rinsed into a capacious porcelain crucible with water. The small portion still adhering to the paper is dissolved in a little warm ammonium sulphide and the solution allowed to flow into the crucible. The solution is evaporated on the water bath after the addition of a few cc. of concentrated nitric acid. If sulphur separates, a little liquid bromine is added when the solution has become quite concentrated. When the globule of sulphur has disappeared, expel the excess of nitric acid by heating on the hot plate or with the Bunsen burner, finally heating to full redness. Cool a little, sprinkle some ammonium carbonate over the precipitate, and ignite again to completely expel sulphuric acid and weigh as antimony tetroxide, $Sb_2O_4$.

The antimony may also be weighed as the trisulphide, $Sb_2S_3$. The precipitate is filtered on a weighed Gooch crucible, and heated to 230° C. in a stream of carbon dioxide to exclude oxygen until constant. Antimony may be determined volumetrically with accuracy. Consult chapter on antimony.

**Tin.** — To precipitate the tin in the filtrate from the antimony the excess of hydrochloric acid is neutralized with ammonia, the solu-

tion diluted somewhat, warmed, and hydrogen sulphide passed until the tin is entirely precipitated. The stannous sulphide is washed with water containing hydrogen sulphide and a few grams of ammonium sulphate. It is dried and detached from the paper which is burned. The precipitate and the ash are placed in a weighed porcelain crucible and heated very gently with free access of air until sulphur dioxide ceases to be given off. The oxidation may be assisted by the addition of a few drops of nitric acid. Finally the precipitate is strongly heated to expel sulphuric acid, which is completely removed by the addition of a little ammonium carbonate and again igniting. It is weighed as stannic oxide, $SnO_2$.

An excellent volumetric method for tin is given in the chapter on the subject. See page 577 and also on page 581.

**Arsenic.** — As only a trace of arsenic is present, a 5 or 10 gram portion of the alloy should be taken for its determination. Dissolve in hydrochloric acid and potassium chlorate and warm to expel the chlorine. Filter off the lead chloride on asbestos and wash a few times with dilute hydrochloric acid. Add one-third the volume of concentrated hydrochloric acid and pass hydrogen sulphide. Filter off the precipitate consisting of the sulphides of copper and arsenic on asbestos, wash with hot water containing hydrogen sulphide and a little hydrochloric acid. Dissolve the arsenic by washing the precipitate with a little warm dilute ammonia. Evaporate the solution nearly to dryness in a porcelain dish. Oxidize the arsenic by warming with concentrated nitric acid, dilute the solution somewhat, neutralize with filtered ammonia, and add magnesia mixture. After standing twenty-four hours filter, wash, ignite, and weigh as magnesium pyroarsenate according to the directions given in chapter on Arsenic.

Arsenic may be determined volumetrically by direct distillation with HCl gas. The volatile arsenious acid being absorbed in water and titrated with iodine according to the methods described in the chapter on arsenic.

## ANALYSIS OF BRASS OR BRONZE

### Alloy of Lead, Copper, Tin, and Zinc, with Small Amounts of Arsenic, Antimony, Cadmium, and Iron

**Solution of the Alloy.** — Weigh out 1 gram of the alloy and place in a 300 cc. beaker, add 10 cc. of concentrated nitric acid and 5 cc. water. Cover the beaker with a watch-crystal and place in a dish of cold water. After one-half hour place the beaker on the water bath and evaporate the solution to dryness. One hundred cc. of boiling water and a few drops of nitric acid are added and the solution boiled for five minutes.

**Tin.** — The stannic oxide is filtered off and washed with hot water. The moist precipitate is introduced into a weighed porcelain crucible and the paper burned in the usual manner. If the amount of tin is small (less than 1%) it is weighed at this point, otherwise it is fused with six times its weight of a mixture of equal parts of sulphur and sodium carbonate. The fused mass is dissolved in hot water and the solution filtered. The **copper, lead,** and **iron** which were carried down with the stannic oxide will remain on the paper as sulphides, while the filtrate will contain all of the tin and any **arsenic** or **antimony** which may have been present. The insoluble sulphides are dissolved in a little nitric acid, the paper washed, and the solution added to the filtrate from the stannic oxide.

If arsenic and antimony are absent, the tin may be precipitated out of the sodium sulphide solution and weighed. The excess of sulphur should first be removed from the solution by heating to boiling after the addition of caustic soda and then adding hydrogen peroxide in small quantities until the solution is nearly decolorized. It is then acidified with hydrochloric acid while stirring constantly, heated, and hydrogen sulphide passed. The stannic sulphide is washed with hot water containing ammonium acetate and a little acetic acid. It is ignited and weighed as stannic oxide in the usual manner.

**Arsenic and Antimony.** — If arsenic is present in the alloy, a small amount of this element will be present in the sodium sulphide solution of the tin and will be precipitated with the stannic sulphide. It may be removed by treating the precipitate with a little concentrated solution of ammonium carbonate and washing. The solution of arsenic should be added to the nitric acid solution of the alloy.

If antimony is also present in the alloy, the sulphide of arsenic, antimony, and tin must be separated by one of the methods given under Analysis of Type Metal.

**Distillation Method for Determination of Arsenic in Brass.** — If arsenic is present in amounts less than 0.10 per cent, 100 gram sample is taken and dissolved in 400 cc. $HNO_3$ (sp.gr. 1.42). The fumes are expelled by boiling and the solution diluted with water to 500 cc.

$NH_4OH$ is added until a slight precipitate of copper hydroxide forms; about 5 grams of $Fe_2(SO_4)_3$ and just enough $NH_4OH$ to cause precipitation are added, the solution diluted to 1000 cc. and boiled, then again diluted and the precipitate allowed to settle several hours. The clear solution is decanted off and the $Fe(OH)_3$ containing all the arsenic and antimony is washed, dissolved in hot HCl, about 2 cc. of hypophosphorous acid added and the arsenic distilled according to the procedure described on page 101, omitting the addition of $Cu_2Cl_2$. Arsenic may now be determined in the distillate by titration with iodine.

If antimony is desired in the analysis it may be obtained in the residue remaining in the flask.

If arsenic is present in amounts over 0.10 per cent, 5 grams of the alloy are dissolved in 20 cc. of $HNO_3$ (sp.gr. 1.52) and then evaporated with 15 cc. of $H_2SO_4$ (sp.gr. 1.84) to fumes. Concentrated HCl may now be added, together with 2 cc. of 30% hypophosphorous acid and the arsenic distilled and determined as outlined above.

**Lead.** — To the filtrate from the stannic oxide, 5 cc. of concentrated sulphuric acid are added and the solution evaporated in a porcelain dish until the nitric acid is entirely expelled and white fumes of sulphuric acid are given off. The solution is cooled by floating the dish on cold water and diluted with 75 cc. of water. Lead is now determined as $PbSO_4$.

**Determination of Cadmium in Brass.** — Ten grams of drillings are dissolved in $HNO_3$ (sp.gr. 1.42), 50 cc. of $H_2SO_4$ (sp.gr. 1.84) added and the mixture evaporated to fumes. The cooled mixture is diluted to 200 cc. with water and boiled. The precipitate is allowed to settle (several hours) and filtered off. The solution containing the cadmium is treated, boiling hot, with $H_2S$ for thirty minutes, the precipitated sulphides filtered off and washed with hot water. The precipitate is dissolved in 400 cc. of 10 per cent $H_2SO_4$.

After boiling, the hot solution is filtered, cooled and treated with $H_2S$ for ten minutes. $NH_4OH$ is added cautiously until ZnS begins to precipitate. The solution is again treated with $H_2S$ for about five minutes, whereupon CdS is completely precipitated. The sulphide is purified by redissolving in 100 cc. of 10 per cent $H_2SO_4$ applying heat. The solution is filtered, diluted to 300 cc. and again treated with $H_2S$. Ammonia is added drop by drop until the cadmium sulphide is completely precipitated. The treatment is repeated to remove traces of impurities and the CdS then weighed in a tared Gooch crucible after drying for two hours at 110° C.

$$\text{Weight of CdS} \times 0.778 = \text{weight of cadmium.}$$

The **copper** is best determined electrolytically. The filtrate from the lead sulphate is heated on the hot plate until most of the alcohol is expelled. Two cc. of concentrated nitric acid are added and the warm solution (about 60° C.) electrolyzed with a current of $\frac{1}{2}$ to 1 ampere

for about six hours. If a gauze electrode is used or one of the electrodes is rotated the time required is very much reduced.

Hydrogen sulphide is passed through the acid filtrate from the copper to precipitate traces of *arsenic*, *antimony*, or unseparated *tin* which may be present.

**Iron.** — The filtrate from the copper is boiled to expel hydrogen sulphide and a little nitric acid added to oxidize the iron, which is precipitated with ammonia and weighed as oxide. If more than a small amount of iron is present, the precipitate must be redissolved and reprecipitated to separate it completely from the zinc.

**Zinc.** — The filtrate from the iron is evaporated to small bulk and the zinc precipitated and weighed as pyrophosphate. The zinc may also be precipitated and weighed as sulphide, or determined volumetrically by titration with potassium ferrocyanide. See chapter on zinc.

### Determination of Copper and Lead Simultaneously by the Electrolytic Method (For Samples Containing over 0.2 Per Cent of Lead)

**Method.** — In a 150 cc. beaker dissolve 1 g. of bronze in 10 cc. of $HNO_3$, sp.gr. 1.42. When the action has ceased, evaporate the solution to dryness, and bake thoroughly on the edge of a hot plate. Add 10 cc. of $HNO_3$, sp.gr. 1.42, and after digesting for a short time add 50 cc. of distilled water, heat to boiling, and allow to stand and settle for about one hour, keeping the temperature just below the boiling point. Filter on double 7 cm. filter papers, keeping the solution hot, and receive the filtrate in a 200 cc. electrolysis beaker. Wash with boiling hot water, dilute to about 100 cc. and insert electrodes. In the positive terminal insert one of the platinum gauze anodes previously described, and in the negative terminal insert a platinum gauze cathode. Cover with a pair of split watch-glasses and electrolyze, using a current of from 3 to 5 amperes at approximately 10 volts for each solution. After about 45 minutes the lead will have been entirely deposited on the anode as $PbO_2$; without interrupting the current add to the electrolyte 3 to 4 cc. of $H_2SO_4$, sp.gr. 1.84, and continue the electrolysis. When the solution is colorless, wash down cover glasses, electrodes and sides of beaker, raising the level of the liquid slightly, and continue the passage of the current about 15 minutes, noting whether or not copper is deposited on the newly exposed surface of the platinum. If no copper appears, transfer about 1 cc. of the colorless solution to the cavity of a porcelain test plate, and add a few drops of fresh $H_2S$ water. If the slightest discoloration occurs continue the electrolysis until there is no discoloration whatever upon repeating the test. Remove the solution from the electrodes quickly without interrupting the current. Rinse the electrodes in distilled water and then dip them in two successive baths of alcohol. Dry the anode at 210° C. for one-half

hour. Weigh as $PbO_2$, using the factor for lead 0.8643 instead of the theoretical value. Shake off the excess alcohol from the cathode and ignite the remainder by bringing it to the flame of an alcohol lamp. Keep the cathode moving continually while the alcohol burns. Weigh as metallic copper.

*Accuracy.* — Duplicate copper determinations should check within 0.10 per cent of copper. Duplicate lead determinations should check within 0.02 per cent of lead. Lead results obtained by this method are likely to be about 0.01 per cent too high.

## SLAG ANALYSIS

The slags made in metallurgical operations consist of complex mixtures and solid solutions of silicates, oxides, aluminates, fluorides and many other compounds. In the molten condition some of these components are probably in igneous solution in each other, their exact composition and the nature of their association depending upon the state of equilibrium at the time the slags were produced. The composition of slags is important both because of its influence upon furnace operations and because of its effects upon the character of the metallic products. For these reasons it is necessary to make frequent slag analyses in all metallurgical plants.

In iron blast-furnace slags the principal constituents are silica, alumina, lime and magnesia, with small amounts of iron oxide, manganese oxide, calcium sulphide and phosphoric acid. Titanium oxide is also frequently present. In modern blast-furnace practice, which involves the use of high lime slags, in order to keep sulphur out of the iron, the percentage of lime and sulphur in the slags is closely watched. In open-hearth furnace slags the amount of phosphorus may be high enough to warrant the sale of the slag as fertilizer.

Lead blast-furnace slags consist mainly of silica, iron oxide, manganese oxide, lime, alumina and zinc oxide, with small percentages of magnesia, barium oxide, lead, copper and sulphur. Of these the most important to the metallurgist are silica, iron oxide, lime, zinc oxide and lead, and determinations of them must be made at least once a day. The other components are determined less frequently. In some of the Mexican lead-smelting plants calcium fluoride occurs in the blast-furnace slags. The lime combined as fluoride is determined separately, as it is not available for the saturation of silica.

### Composition of Slags

**Blast-Furnace Slags.** — $SiO_2$ = 35 to 45%; FeO = 0.2 to 0.5%; CaO = 32 to 46%; $Al_2O_3$ = 14 to 17%; MgO = 1.0 to 1.5%; $MnO_2$ = trace to 0.1%; S = 1.5 to 2.0%; $P_2O_5$ = 0.01 to 0.96%.

**Lead Blast-Furnace Slags.** — $SiO_2$ = 36.7%; FeO = 29.5%; CaO = 20.9%; $Al_2O_3$ = 3.16%; MgO = 1.69%; MnO = 0.91%; S = 0.75%; BaO = 0.54%; ZnO = 4.19%; Pb = 1.38%; Cu = 0.10%; Au = 0.001%; Ag = 0.70%.

Average of one year's analyses on representative samples.

**Copper Blast-Furnace Slags.** — $SiO_2$ = 23 to 49%; Fe(MnO) = 2.5 to 57%; Ca(MgO) = 2.5 to 25%; $Al_2O_3$ = 1.5 to 18%; ZnO = nil to 23%; Cu = 0.15 to 1.1%; S = nil to 1.5%.

Copper slags are made up mainly of silica, iron oxide, lime and alumina. The manganese oxide and the zinc oxide are usually less than in lead slags. The silica and alumina, however, are generally higher. This is especially true in the case of reverberatory slags, in which a greater viscosity can be permitted. The percentage of copper is quite important as it measures the chief source of loss of that metal. The percentage of copper in the slag is usually about one hundredth of that in the matte. The amount of lime in copper slags varies a great deal more than it does in lead slags, as it is of less importance in influencing the metallurgical results. In converter slags the copper may amount to several per cent, and the slag then becomes an important by-product.

### Decomposition of the Sample

**General Reverberatory Slag.** — Usually 0.5 gram of the finely ground slag is taken for a determination, a larger amount when the constituents sought are present in very small amount. The material placed in a platinum crucible is fused with 5 to 6 grams of $Na_2CO_3$ at red heat (muffle furnace, if possible) for 10 minutes. The mass is cooled on the side of the crucible, and the fusion dissolved in a casserole by adding an excess of HCl, followed by a few cc. of $HNO_3$. The solution is evaporated to dryness and the residue baked. The mass is taken up with dilute HCl. Silica remains as a residue and is filtered off and determined. The metals are determined in the filtrate.

**Chilled Blast Furnace Slag.** — The sudden chilling of the molten slag by dropping into water causes a physical change in the material which enables a decomposition by means of acids without resort to fusion, as given above.

About 0.5 gram of the finely ground chilled slag in a small casserole is moistened with water and about 3 cc. of concentrated HCl added. All lumps are broken up by stirring with a glass rod until a smooth jelly results. A few drops of $HNO_3$ are added to oxidize the iron and the jelly is worked up around the sides of the casserole in an even layer to the height of about $\frac{1}{2}$ inch. (This permits rapid dehydration of the silica and reduces loss by "spitting".) The acids are expelled by evaporation and the residue gently baked. (If the temperature is too high some alumina will combine with the silica and give high results for $SiO_2$.) After cooling, about 20 cc. of concentrated HCl are added and the mixture boiled for a few minutes, then diluted with an equal volume of hot water and filtered hot. $SiO_2$ remains as a residue, the metals are in solution.

**Silica.** — The residue obtained from the decomposition is washed with hot water until free from chlorides, the washings being added to the main filtrate. The residue and filter are ignited, then cooled and weighed as $SiO_2$.

NOTE. — Should barium be present, as is the case with many lead slags, nitric acid is omitted in the decomposition, as this would cause contamination

of the silica with barium sulphate. If nitric acid is used it is advisable to obtain the silica by difference, by first weighing the residue. This is placed in a weighed platinum dish, then treated with hydrofluoric acid and a dew drops of sulphuric acid. The solution is evaporated, all the acids and the silica being expelled (as silicon fluoride). Any remaining residue is weighed and subtracted from the first weight obtained. The loss represents the $SiO_2$.

Copper slags carrying 40 to 45 % of $SiO_2$ are more troublesome than those with 35 to 37 % of $SiO_2$ in regard to alumina uniting with the silica during dehydration.

**Lime.** — (In presence of iron oxide and alumina) Ammonia is added to the filtrate from silica and then oxalic acid little by little until the precipitated iron and aluminum hydroxides just dissolve. The solution is again made ammoniacal and oxalic acid again added to dissolve iron. The solution should appear a light apple-green color. It is now boiled for a few minutes and the precipitated calcium filtered off and washed with hot water until free from oxalic acid, six or seven times being generally sufficient.

The filter containing the calcium oxalate is dropped in a beaker, 150 cc. of hot water added together with 15 cc. of (1 : 1) $H_2SO_4$ and the oxalic acid titrated with standard potassium permanganate.

1 cc. of 0.1 N $KMnO_4$ = 0.0028 gram of CaO.

The Fe value of $KMnO_4$ multiplied by 0.5 = CaO value.

Notes. — If preferred iron and aluminum may be precipitated as hydroxides, and filtered off, calcium being determined in the filtrate. It is advisable to redissolve the precipitate to recover any occluded lime and again precipitate the hydroxides with ammonia, the filtrate being combined with the main filtrate.

In place of titrating the oxalate of lime, it may be ignited and the residue weighed directly as CaO.

If oxalic acid is added in the form of a fine powder instead of a solution the calcium precipitates in a much more granular form and requires less boiling before filtering.

**Iron.** — (In presence of silica) Half a gram or more of the finely ground chilled slag in a beaker is treated with 50 cc. of boiling water, the particles stirred up and kept in suspension and about 25 cc. of concentrated HCl added. The solution is boiled until clear. (If coke dust is present it will still be evident, but may be neglected.) Stannous chloride solution is added, drop by drop, until the iron is reduced (solution becomes colorless) and 2–3 drops excess added. The solution is cooled by placing the beaker in cold water. Mercuric chloride, $HgCl_2$, solution is added to precipitate the excess of stannous chloride.

The iron is determined by titration with standard potassium dichromate using ferricyanide indicator on a spot plate. See subject in the chapter on Iron. Report as FeO.

1 cc. of 0.1 N $K_2Cr_2O_7$ = 0.00558 g. of Fe, 0.00719 g. of FeO

Fe $\times$ 1.2865 = FeO

Note.— The iron may be precipitated as hydroxide, then dissolved in dilute $H_2SO_4$, the solution reduced by boiling with test lead or reduced in cold

solution with zinc and the solution titrated with standard potassium permanganate. This method is frequently preferred where previous fusion to decompose the ore has been required. Lime may be determined in the filtrate from iron.

## OTHER CONSTITUENTS IN SLAGS

**Alumina.** — *Phosphate Method.* — The filtrate from the silica determination is diluted to about 400 cc. with cold water and 30 cc. of 10% ammonium phosphate added. Dilute ammonia water is added until a slight permanent precipitate forms.

1.5 cc. of concentrated HCl is added and 40 cc. of 20% solution of $Na_2S_2O_3$ and the mixture boiled for about two or three minutes. 15 cc. of 20% ammonium acetate and 6 cc. of strong acetic acid are added and the boiling continued for about 15 minutes.

The precipitate is allowed to settle for 15–20 minutes, the clear solution decanted through a filter and finally the aluminum phosphate filtered and washed. (The presence of the acetate makes the compound more granular.) 10 washings with hot water are sufficient.

The precipitate is dried, ignited and weighed as $AlPO_4$.

The precipitate contains 41.85% $Al_2O_3$.

Note. — The slag may be decomposed by treating 0.5 gram in a platinum dish with 5 cc. $HNO_3$, 6 cc. of HF and about 2 cc. of (1:1) $H_2SO_4$. The sample is taken to strong fumes of $SO_3$, then cooled and 10 cc. of HCl added and the mixture boiled. Alumina and iron may now be precipitated as hydroxides, and filtered off and washed. After dissolving in HCl precipitate $AlPO_4$ as in the method above.

**Manganese.** — Half a gram of the slag is placed in a beaker and about 50 cc. of water added, the solution stirred until the material is in suspension and about 15 cc. of HCl added, followed by 5 cc. of $HNO_3$ and the solution boiled until most of the chlorine has been expelled.

Hot water is added to make up to a volume of about 100 cc. The iron is now precipitated by adding ZnO emulsion until the acid is neutralized and an excess of ZnO forms on the bottom of the beaker.

The solution is boiled for a few minutes and the manganese titrated while the solution is still hot (in presence of the precipitate) with standard potassium permanganate.

The end-point is best seen by allowing the precipitate to settle slightly and observing the clear upper stratum of the liquid.

1 cc. of 0.1N $KMnO_4$ = 0.00165 g. of Mn.

The lime value of the $KMnO_4 \times 0.588$ = Mn.

Note. — In place of the method given above consult the chapter on Manganese for the volumetric oxalic acid method.

**Zinc.** — To 0.5 gram (1 gram if zinc is low) of the sample in a casserole is added 3 cc. of water, 5 cc. of HCl and 2 cc. of $HNO_3$. When the $SiO_2$ is completely gelatinized about 4 grams of $NH_4Cl$ is stirred in.

The sample is dehydrated only until the residue crumbles easily as baking is liable to volatilize some zinc as chloride. About 30 cc. of hot water are added and the solution brought to boiling, filtered and the residue washed with hot water.

To the filtrate ammonium persulphate and bromine are added the amount being governed by the manganese present, i.e., 0.03 g. of ammonium persulphate and 10 cc. bromine for every 0.01 g. of Mn in solution. Ammonia is added in slight excess, the solution boiled about 2 minutes, filtered, and the residue, $MnO_2$, etc., washed. (It is advisable to redissolve the precipitate in a little dilute HCl and again precipitate with persulphate and bromine, adding the filtrate to the main filtrate.)

The solution is just neutralized with HCl and 5 cc. excess added, followed by 2 grams of test lead. The solution is boiled about 15 minutes.

About 8–10 cc. of HCl are added, the solution heated to about 60° C. and the potassium ferrocyanide added. When the titration is almost completed the bluish-white color of the precipitate changes to nearly pure white.

If the ferrocyanide is made up by adding 21.63 grams of potassium ferrocyanide per liter of solution, 1 cc. will equal very nearly 0.005 gram of Zn. Consult chapter on Zinc.

In place of the above method the rapid method given in the chapter on Zinc may be followed.

**Magnesia.** — 0.5 gram or more of the finely ground chilled slag, placed in a casserole is moistened with water, 5 cc. of HCl and a few drops of $HNO_3$ added. The acids after reacting with the slag are evaporated off and the silica dehydrated. The residue is taken up with 15 cc. of HCl and about 30 cc. of water, and boiled.

Silica is filtered off and washed.

The filtrate is made slightly alkaline with ammonia, 8 cc. of $(NH_4)_2S$ and 1 gram of $(NH_4)_2CO_3$ added and the solution boiled for a few minutes, the precipitate then filtered off and washed several times with water containing a little $(NH_4)_2S$.

The filtrate is made slightly acid with HCl and boiled down to about 50 cc. The precipitated sulphur is filtered off and the filter washed. If the solution is cloudy it is cleared by adding bromine water and boiling.

Ammonia is now added and a small amount of ammonium oxalate to remove any CaO still remaining; after boiling, the oxalate of calcium ("lime") is filtered off and washed.

Magnesia is now precipitated in the filtrate by addition of $Na_2HPO_4$ or another alkali phosphate, and the magnesium ammonium phosphate filtered off, washed with 2% ammonium nitrate

solution, ignited and weighed as $Mg_2P_2O_7$. Consult the chapter on Magnesium.

$$Mg_2P_2O_7 \times 0.3621 = MgO$$

**Copper.** *Colorimetric Method with Ammonia.* — The percentage of copper normally present in blast furnace slags should not exceed 0.3 per cent. Converter slags may contain as much as 2.5 per cent copper. The colorimetric method is especially adapted for this determination owing to its simplicity and speed.

Slags which have been "chilled" are *readily* decomposed by HCl. Stirring constantly during the acid action and diluting as soon as decomposition is complete prevents the separation of gelatinous silica and hastens the solution of copper.

**Procedure.** — *Color Standards.* 0.2 gram of pure copper foil is dissolved in 20 cc. of 1 : 1 $HNO_3$ in a covered beaker, warming gently. After evaporating down to about 10 cc., the solution diluted to 50 cc. is transferred to a graduated liter flask, 200 cc. of ammonium hydroxide added and the solution diluted to 1000 cc.

5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 cc. portions are taken and placed in 100-cc. Nessler colorimetric tubes. (In place of the tubes clear white glass bottles of about 150 cc. capacity may be used.) The volume of each solution is diluted to 100 cc. with 1 : 5 ammonium hydroxide.

If a colorimeter is available a standard is taken that corresponds to that of the sample as prepared according to directions below and comparisons made by viewing the solutions through the depth of solutions adjusted to give the same intensity of color.

**Preparation of the Sample.** — Two grams of the finely crushed sample (100 mesh) is treated in a beaker with 10 cc. of water to thoroughly moisten the powder, 10 cc. of strong HCl are added and the mixture stirred, warming gently until the undissolved residue becomes flocculent, remaining in suspension.

About 90 cc. of $H_2S$ water are added or the same volume of water and $H_2S$ gas passed in until the solution is saturated. The solution is warmed gently until the copper sulphide coagulates. The precipitate is filtered through a small filter (Witt filter is O.K.) and washed with $H_2S$ water.

The sulphide is now dissolved in 5 cc. strong $HNO_3$ (in the beaker in which the CuS was precipitated) 30 cc. 1 : 5 $NH_4OH$ solution are added, the solution filtered through a second filter, and this washed with 1 : 5 ammonia reagent.

The copper solution is transferred to a Nessler tube (bottle or colorimeter tube as the case may require) and comparison made with a standard, the solution being made up to 100 cc. with 1 : 5 $NH_4OH$.

### ELECTROLYTIC AND IODIDE METHODS FOR COPPER

For extreme accuracy the electrolytic or iodide methods are recommended. Details of these methods may be found in the chapter on Copper. See also the chapter on Fire Assay Methods by I. A. Palmer.

**Lead.** — The determination of lead is frequently required in slags. Slags high in silica are apt to contain lead in appreciable quantities, probably combined as silicate. The decomposition of the slag by treatment with HF as given in the foot note on page 691 is recommended.

The determination of lead in slag does not differ materially from its determination in ores. Reference is made to the chapter on Lead for its estimation.

**Other Constituents.** — The determination of barium, titanium, sulphur, phosphorous, chromium, cobalt, nickel, alkalies, etc., are occasionally necessary. The procedures for these determinations may be found in the chapters dealing with the elements in question.[1]

[1] The introduction to this section "Slag Analysis" was written by Prof. I. A. Palmer, Department of Metallurgy, Colorado School of Mines.

## THE FIRE ASSAY FOR GOLD AND SILVER[1]

**Definitions.** — *Fire assaying* is a branch of quantitative chemical analysis in which metals are determined in ores and metallurgical products by extracting and weighing them in the metallic state. The methods employed involve slag-melting temperatures and the use of reducing, oxidizing and fluxing reagents, and are in principle the same as those used in metallurgy.

The metals ordinarily determined by fire assaying are gold, silver and platinum. Antimony, bismuth, lead and tin can be determined in this way also, but the results are usually more or less inaccurate.

An *ore* is a mineral aggregate from which one or more metals can be extracted at a profit.

*Metallurgical products* include a large number of metal-bearing mixtures and compounds, ranging from high grade gold and silver bullion to very weak cyanide and sulphate solutions.

The constituents of an ore are usually divided into two general classes, the valuable minerals containing the *metals*, and the non-valuable minerals or *gangue*. A similar classification can be made in the case of many metallurgical products. In gold and silver bullion and other alloys all of the components are metallic, and the assaying problems involve simply the separation of metals.

### GENERAL OUTLINE

With ores and metallurgical products containing non-metallic elements the process consists, briefly, in the production of two liquids, liquid lead containing the valuable metals, and liquid slag containing the waste matter or gangue. The two liquids separate from each other by reason of the great difference in specific gravity. The valuable metals are separated from the lead and from each other by taking advantage of differences in chemical properties. The slag is discarded.

In the operation of the process the gold and silver, and platinum, if present, are collected from the metal-bearing portion of the ore or metallurgical product by means of molten lead reduced from litharge or lead oxide. The gangue is converted into a fusible slag by means of reagents known as fluxes.

The effectiveness of the fire assay in separating gold, silver and platinum from ores and metallurgical products depends upon two properties of these metals; first their weak affinity for non-metallic elements, especially at high temperatures, and second, their very

[1] By Irving A. Palmer, Professor of Metallurgy, Colorado School of Mines.

great affinity for molten lead. The collection of the precious metals in the lead, therefore, is the simplest part of the process. The fluxing of the gangue is much more difficult, and requires considerable knowledge and skill. If the fluxing is properly performed the collection of the valuable metals usually takes care of itself.

**Reagents.** — A flux is a substance which when heated in contact with some difficultly fusible compound, either combines with it or takes it into solution, in each case producing a compound or mixture which is easily fusible at ordinary furnace temperatures. The principal fluxes and other reagents used in fire assaying are described in the following paragraphs.

**Litharge** or oxide of lead, PbO, melting point 883° C., has several important uses. It furnishes the lead which collects the precious metals; it readily combines with silica, producing easily fusible silicates; and it acts as an oxidizing and desulphurizing agent. It is a very strong basic flux.

**Sodium carbonate,** $Na_2CO_3$, melting point, 852° C., is a powerful basic flux. It combines with silica and alumina, producing fusible silicates and aluminates. When molten it has the property of dissolving or holding in suspension a number of refractory gangue materials. To some extent, also, it acts as an oxidizing and desulphurizing agent. Potassium carbonate, $K_2CO_3$, melting point 894° C., is rarely used in fire assaying because of its greater cost.

**Borax glass,** $Na_2B_4O_7$, melting point 742° C., is an acid flux used for combining with or dissolving the basic and some acid constituents of the gangue, producing easily fusible complex borates and mixtures of borates and other compounds. Even silica dissolves to some extent in molten borax glass.

**Silica,** $SiO_2$, melting point 1755° C., is a strong acid flux. It combines with metallic oxides and produces silicates which in many cases are considerably more fusible than silica itself.

**Granulated lead** or **test lead** is used in the scorification assay, which is conducted under oxidizing conditions, and in which, therefore, litharge could not be employed as a source of lead.

**Lead foil** or **sheet lead** is used in the assay of gold and silver bullion. It, as well as the granulated lead, should be free from silver and bismuth.

**Flour** is known as a reducing agent. It contains carbon, which reduces lead from litharge. Charcoal was formerly used for this purpose, but it is not so convenient.

**Argol** or **crude cream of tartar,** $KHC_4H_4O_6$, is both a basic flux and a reducing agent. On being heated it decomposes as follows: $2KHC_4H_4O_6 + \text{heat} \rightarrow K_2O + 5H_2O + 6CO + 2C$. It is effective in assays requiring strong reducing action and low temperatures.

**Iron** is sometimes used as a desulphurizing and reducing agent. It decomposes most of the heavy sulphides, yielding the metals and iron sulphide.

**Potassium nitrate,** $KNO_3$, melting point 339° C., is a powerful oxidizing agent. It is used to neutralize the effect of an excess of reducing substances in the material to be assayed. High sulphur ores, if assayed without previous roasting, require the addition of nitre to the charge. In contact with a reducing agent two molecules of potassium nitrate give up five atoms of oxygen, as shown in the following equation:

$4KNO_3 + 5C \rightarrow 2K_2CO_3 + 3CO_2 + 2N_2$. The potassium oxide coming from the decomposition of the nitre acts as a basic flux.

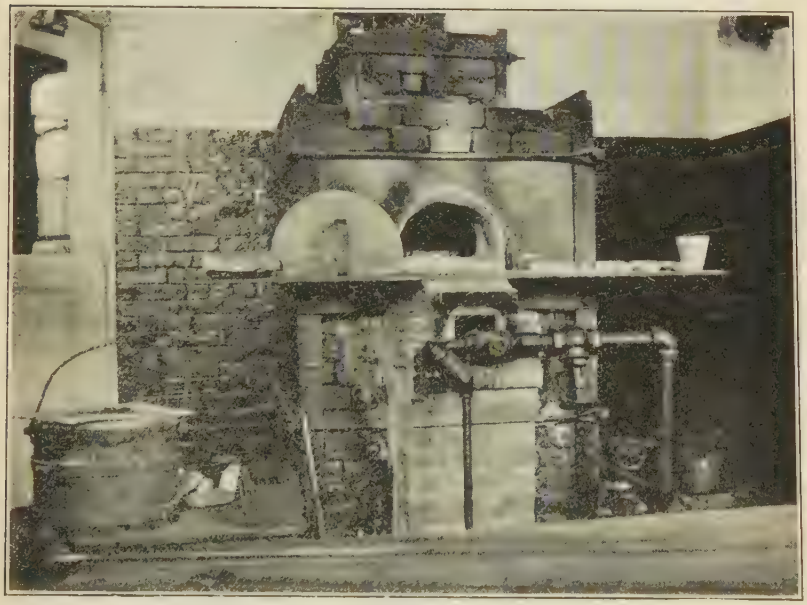


Fig. 126. Oil Muffle Furnace.

**Common salt,** NaCl, melting point 819° C., is a neutral substance sometimes used as a cover for crucible fusions to exclude the air. When molten it rests on top of the charge and does not enter into it.

All of the reagents used must be pure and in a finely divided condition. Sodium carbonate shows a tendency to form lumps. These should be broken up and the entire mass put through a moderately fine screen.

**Furnaces and Equipment.** — The major operations in fire assaying are usually conducted in muffle furnaces. The muffle is a box-like receptacle made of fire clay, so placed in the furnace that it is heated on top, bottom and all sides except the front. In it are

placed the refractory vessels containing the material to be assayed. There is thus no direct contact with the fuel or products of combustion. The fuel used may be coal, oil, gasoline or gas. See Figures 126, 127, 128.

**Cupels.** — The separation of the precious metals from the lead alloys produced in fire assaying is effected in small shallow vessels of bone ash, known as *cupels*. The material consists mainly of calcium phosphate, with small percentages of magnesium phosphate, calcium

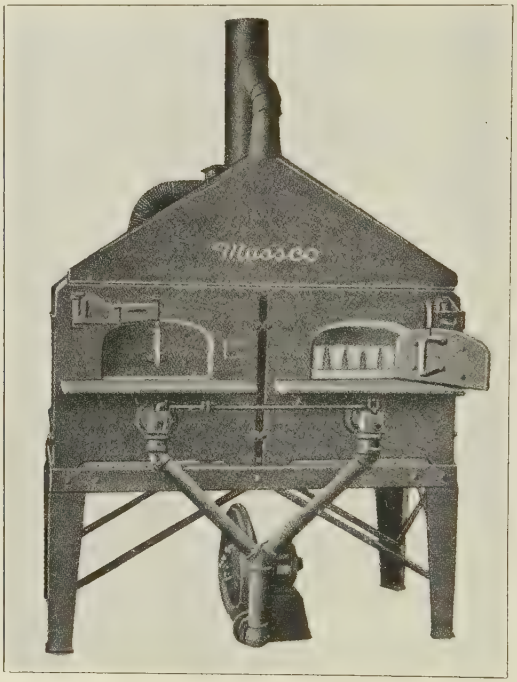


Fig. 127. Muffle Furnace.

fluoride and calcium carbonate. It is a product of the burning of animal bones, preferably those of the sheep. It should be ground fine enough to pass a 40 mesh screen, in which case about 50 per cent of it will pass a 150 mesh screen. The cupels are made by moistening the bone ash with a small amount of water and then compressing it in the cupel mould, which consists essentially of a ring and die. The bone ash is forced into the shape desired at a considerable pressure, so as to insure sufficient rigidity in the cupel. The amount of water needed varies, but should be as low as possible.

The cupels should be dried very slowly, so as to avoid cracking. By using high pressures good cupels can be made from perfectly dry bone ash. See under group Fig. 130.

The requirements of a good cupel are that it should be infusible at ordinary furnace temperatures, that it should not be attacked by metallic oxides, that it should be porous, and that it should be sufficiently rigid to permit of considerable handling.

Cupels can be made of Portland cement, magnesia, or of mixtures of these materials with bone ash. They are considerably cheaper but not so satisfactory as those made of bone ash alone.

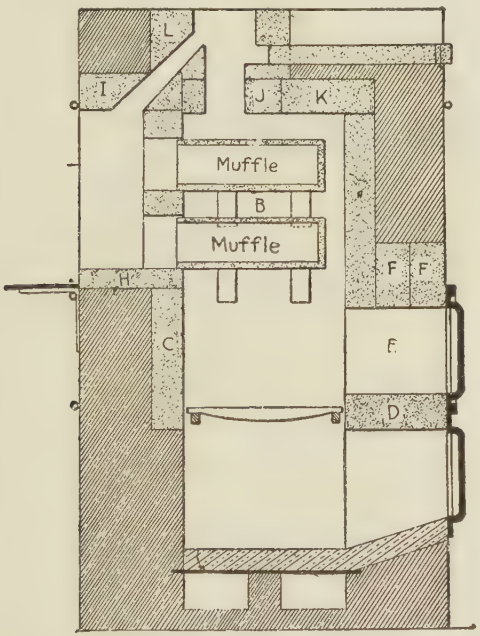



Fig. 128. Cross Section of Two Muffle Assay Furnace.

**The Assay-Ton System.** — As the precious metals are bought and sold by the Troy system of weights and measures, and ores by the Avoirdupois system, considerable time would be lost in calculating assay results, were there no way of avoiding it. To simplify the calculation Prof. C. F. Chandler, of Columbia University, invented the assay-ton system of weights. The assay-ton is equal to $29.166\frac{2}{3}$ milligrams. As there are $29{,}166\frac{2}{3}$ Troy ounces in an Avoirdupois ton of 2,000 pounds the number of milligrams and fractions of a milligram of precious metals found in an assay-ton of ore corresponds to the number of Troy ounces in an Avoirdupois ton.

**Sampling.** — It goes without saying that good results in assaying presuppose accurate sampling. Silver is reported in assay certificates to the nearest tenth of an ounce; gold usually to the nearest one hundredth of an ounce. One tenth of an ounce means one part in 291,667; one hundredth of an ounce, one part in 2,916,667. In the preparation of the sample, therefore, the ratio between the weight of any fractional portion and the weight of the largest particle in it must be very large, so that the accidental inclusion of a number of rich pieces in any portion shall not affect the results beyond the limits of error in assaying. The final pulp sample should be of a fineness ranging from 80 mesh, in the case of low grade silver ores, to as fine as 200 mesh in the case of non-uniform gold ores. Small particles of metallic gold in the material necessitate fine grinding

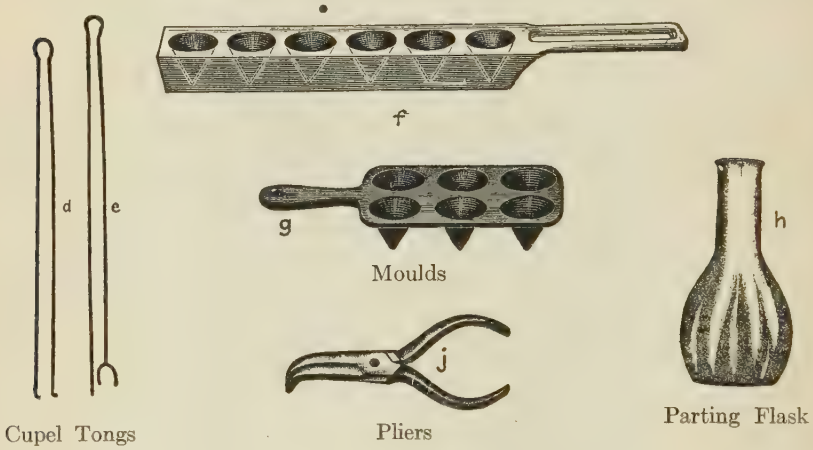



Fig. 129. Apparatus for Fire Assay.

and very thorough mixing. It is a good rule to mix all pulp samples on a rubber cloth before weighing the portions for assay.

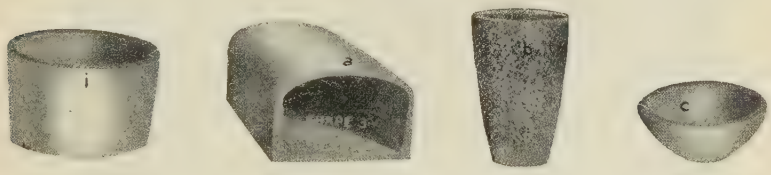
**Balances and Weights.** — The balances used in fire assaying are somewhat different from those found in chemical laboratories. They are known as flux, pulp and assay balances. The assay balances are for weighing the gold and silver, often exceedingly small in amount, and are the most delicate type of commercial balances made. They should be quick in action and not liable to changes in adjustment. The beam should be short, light and rigid. The balance should be sensitive to .01 milligram at least. It need not have a capacity of more than .5 gram but should be accurate with that load.

In large laboratories separate balances are furnished for weighing the gold. These balances should be adjusted before each weighing and should be handled with the greatest of care. In the assay of

gold ores, when using a half assay-ton portion, every error of .01 milligram in weighing the gold means a variation in the value of the ore of forty cents per ton. See Fig. 131 for final weighings.

**The Crucible Assay.** — This method of fire assaying is adapted to the great majority of gold and silver ores and to many metallurgical products. The process consists in treating a weighed portion of the sample, carefully mixed with the necessary reagents, in a fire clay crucible. In order to do this effectively the character of the material to be assayed must be known. Thus, ores may be oxides or sulphides. They may be basic, acid or neutral. They may be strongly oxidizing or strongly reducing. Each case requires a particular method of treatment.

The amount of sample usually taken is one half assay-ton, run in duplicate. Twenty-gram fire-clay crucibles are used, that is, crucibles capable of holding twenty grams of ore and the necessary



Cupel Muffle Crucible Scorifier

FIG. 130. Apparatus for Fire Assay.

reagents. In most cases the total charge will fill the crucible to within one inch of the top.

**Lead Reduction with Oxidized Ores.** — Experience has shown that the best results are obtained when the lead reduced from the charge amounts to from 25 to 30 grams. If the ore is oxidized, a reducing agent must be added to precipitate the necessary lead. Flour is the reagent ordinarily used, although charcoal or argol can be substituted for it. The lead is reduced according to the following equation:

$$2PbO + C \rightarrow 2Pb + CO_2$$

That is, 12 parts of carbon theoretically will reduce 414 parts of lead from litharge. Hence, the theoretical reducing power of carbon is $\frac{414}{12}$ or 34.5. In practice, the reducing power of charcoal is found to range between 25 and 30, and that of flour from 10 to 12. Argol has a reducing power of about 8 or 9. In most oxidized ores, therefore, from $2\frac{1}{2}$ to 3 grams of flour will be required to reduce from 25 to 30 grams of lead from the litharge.

If the ore contains ferric oxide, manganese dioxide, or some other easily reducible oxide, more flour must be added. Some iron-manganese ores require as much as 5 grams of flour to throw down the

necessary lead. With unknown ores the right amount can be determined only by trial.

**Lead Reduction with Sulphide Ores.** — In the case of ores containing sulphides, arsenides or other reducing substances, there will be a reduction of lead without the addition of carbon. In fact it is usually necessary to add an oxidizing agent to prevent the pre-

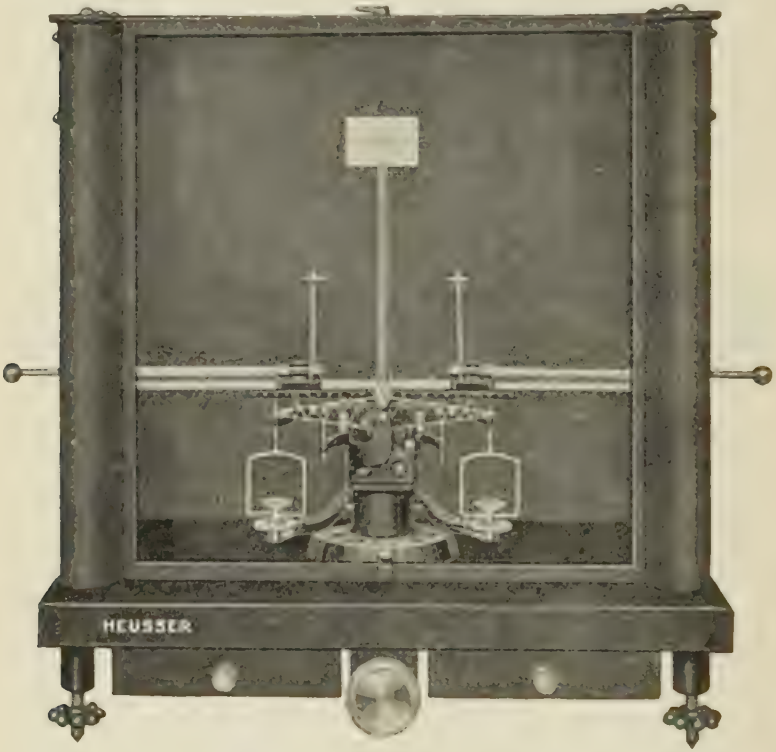



Fig. 131. Assay Balances for Small Weights.

cipitation of too much lead. The following reactions show the effect of a number of sulphide minerals when heated in contact with litharge and sodium carbonate.

(1) $PbS + 3PbO + Na_2CO_3 = 4Pb + Na_2SO_4 + CO_2$.
(2) $ZnS + 4PbO + Na_2CO_3 = 4Pb + ZnO + Na_2SO_4 + CO_2$.
(3) $2FeS_2 + 15PbO + 4Na_2CO_3 = 15Pb + Fe_2O_3 + 4Na_2SO_4 + 4CO_2$.

The sodium carbonate induces the complete oxidation of the sulphur to $SO_3$, with the formation of the very stable compound sodium

sulphate. In the absence of an alkaline carbonate most of the sulphur is oxidized to $SO_2$ only, and the amount of lead precipitated is correspondingly decreased.

Reaction (3) shows that pyrite has a greater reducing power than flour itself. If, therefore, a half-assay-ton of ore consisting mainly of pyrite were to be subjected to a crucible fusion, without the addition of some oxidizing agent, anywhere from 100 to 150 grams of lead would be reduced. This would be entirely too much for the subsequent process of cupellation. In order to prevent the reduction of an excessive amount of lead, potassium nitrate is added to the charge. The following reactions show the oxidizing power of this reagent.

(4) $2KNO_3 + 5Pb = 5PbO + K_2O + N_2$.

(5) $2FeS_2 + 6KNO_3 = Fe_2O_3 + 4SO_3 + 3K_2O + 3N_2$.

Reaction (4) shows that 202 parts of nitre will oxidize 1035 parts of lead to litharge. The theoretical oxidizing power of nitre, as measured against lead, is, therefore, 5.12. Reaction (5) when compared with reaction (3), given above, shows that 606 parts of nitre will oxidize the pyrite needed to reduce 3105 grams of lead from litharge. Here again the oxidizing power of nitre is shown to be 5.12. In practice, it is found to be somewhat less, more nearly 4.5.

The fire assay of sulphide ores, therefore, involves either a preliminary assay, or a calculation from the chemical analysis, in order to determine the amount of nitre to be added. With unknown ores it is better to make a preliminary fusion, using 5 grams of the ore, 75 grams of litharge, 20 grams of sodium carbonate and 10 grams of borax glass. The button of reduced lead is weighed and its weight divided by 5. This gives the reducing power of the ore. From this can be calculated the reducing power of one half assay-ton of the ore, and the amount of nitre necessary to add in order to cut down the weight of the reduced lead to about 30 grams. An excess of silica or borax glass decreases somewhat the amount of lead by causing the formation of difficultly reducible lead silicates or borates.

**Amount of Litharge.** — The amount of litharge for a half assay-ton charge usually ranges from 60 to 75 grams. Only about half of this is needed to produce the 25 to 30 grams of metallic lead used as the collector. The excess litharge serves to prevent the reduction of other base metals, such as antimony, bismuth, iron, copper and zinc, to help flux the silica, to act as a solvent for some of the refractory gangue materials, and to make sure that every particle of the ore in the crucible is in close proximity to one or more particles of litharge. In special cases it may be advisable to use a very large excess of litharge, as in the assay of rich gold telluride ores, zinc precipitates and saturated cupels.

**Amount of Sodium Carbonate.** – The amount of sodium carbonate to be used depends somewhat upon the character of the ore, although the modern practice is to use about the same quantity in assaying a great variety of ores and metallurgical products. The principal function of the sodium carbonate is to flux the silica and alumina, which are nearly always present in greater or less degree. The reactions are as follows:

(6) $Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$.

(7) $2Na_2CO_3 + SiO_2 = Na_4SiO_4 + 2CO_2$

(8) $Na_2CO_3 + Al_2O_3 = Na_2Al_2O_4 + CO_2$

The two silicates and the aluminate are both quite fusible at ordinary furnace temperatures.

The silicates used in assaying and in metallurgy are usually classified according to the ratio between the oxygen in the acid radical and that in the base. Only four of these type silicates are of any practical importance. They are shown in the following table:

| | |
|---|---|
| Sub-silicate | $4RO, SiO_2$ |
| Mono-or singulo-silicate | $2RO, SiO_2$ |
| Sesqui-silicate | $4RO, 3SiO_2$ |
| Bi-silicate | $RO, SiO_2$ |

In the above silicates, the ratios are $\frac{1}{2}$ to 1, 1 to 1, $1\frac{1}{2}$ to 1, and 2 to 1, respectively.

Reactions (6) and (7) show that to flux one part of silica to bi-silicate and mono-silicate requires about $1\frac{3}{4}$ parts and $3\frac{1}{2}$ parts, respectively, of sodium carbonate. If the half assay-ton of ore, therefore, consisted of almost pure quartz, it would take 25 grams of sodium carbonate to flux it to sodium bi-silicate, and 50 grams to flux it to the mono-silicate. As a matter of fact, the bi-silicate slag is satisfactory in this case. In general, the acid silicates have lower melting points but greater viscosity than the basic silicates. The excess litharge in the charge also combines with silica, and may thus produce more basic silicates. At any rate, a mixture of silicates usually has a lower melting point than that calculated from the melting points of its components.

Reaction (8) shows that 1 part of sodium carbonate is required to flux 1 part of alumina.

In practice from 30 to 35 grams of sodium carbonate are used in a half-assay-ton charge. In many cases this may seem to be a large excess. It must be remembered, however, that this reagent serves also to assist in the oxidation of the sulphides through the formation of sodium sulphate, that it has a solvent effect upon refractory oxides and other substances, and that it increases the bulk of the

charge, thus protecting the ore from the action of the air and from the escape of the more volatile metals and their compounds. Being very fusible itself, an excess also serves to increase the fusibility of very refractory charges.

**Amount of Borax Glass.** - The rational formula of borax glass, $Na_2O$, $2B_2O_3$, shows that it is an unsaturated compound and can take up more of the base. This base may be sodium oxide or one or more of the heavier oxides. The result of the addition is a fusible complex borate. This is shown in the following reaction:

(9) $Na_2O, 2B_2O_3 + 5CaO = Na_2O, 5CaO, 2B_2O_3$

The compound produced is a mono-borate and shows the fluxing of 1.4 parts of lime by one part of borax. The solvent power of borax glass for various substances has been referred to above. In practice it does not matter whether there is chemical combination or solution. What is desired is perfect liquidity at furnace temperatures.

The amount of borax glass ordinarily used in a half assay-ton charge varies from 10 to 15 grams. If the ore is very basic and refractory, more borax should be used. As in the case of sodium carbonate an excess of borax glass ordinarily can do no harm, as it is quite fusible.

Some assayers use silica in the assay of very basic ores. It is a good flux for iron and manganese oxides, producing fusible silicates. It is also very cheap. It cannot be used in excess, because of its very high melting point.

**Assay Slags.** — The slags produced in crucible fusions in fire assaying are often very complex mixtures of silicates, borates, oxides and other compounds. In the molten state there can be chemical combination, solution and suspension, all at the same time. Ordinarily it is quite useless to attempt the formation of a definite silicate or borate. If a sufficient amount of the proper fluxes is used, and a high temperature at the finish, there is usually no trouble in getting a good fusion. As a general rule the greater the complexity of the slag the lower its melting point.

### Weighing and Mixing the Charge

It is usually most convenient to mix the charge within the crucible. The fluxes should be put in first, the most bulky one at the bottom. They should be measured rather than weighed, in order to save time. Only the flour and nitre need to be measured accurately. The ore is carefully weighed on a pulp balance and placed on top of the fluxes. The mixing is best done by means of a steel spatula, and should be very thorough. Good mixing is shown by the uniform appearance of the charge. The fluxes should be free from lumps. The practice of using a salt or borax cover on the charge is not so common as it was. Ordinarily it is not necessary. When a salt cover

is used in assaying rich ores, there is some danger of the production of volatile silver and gold chlorides. Borax glass as a cover is expensive.

**Fusing the Charge.** — The fusion of the charge is best conducted in a muffle furnace, although it can be made in a coke furnace, or even in a blacksmith's forge. The crucibles should be placed in the muffle when the latter is at a bright red heat. The temperature is then gradually raised until at the end of 45 minutes it reaches a light yellow heat, say 1150° C. Sulphide ores should be run rather more quickly than oxide ores, so as to oxidize the sulphides before they have a chance to melt down into a matte. If the heat be raised too rapidly there is danger of boiling over, due to the large volume of gases liberated.

The crucible fusion may be divided roughly into three stages. There is first the preliminary heating stage, accompanied by some reduction of lead from litharge, the partial fusion and decomposition of nitre if present, the partial reduction of higher oxides, and some fluxing of silica by sodium carbonate and litharge. During the second stage most of the chemical reactions take place and the entire charge seems to be in a state of violent agitation. Lead is reduced from the litharge by flour, sulphur or other reducing agent, and the multitude of small shots pick up the adjacent particles of gold and silver. Gold tellurides and silver sulphides are decomposed by litharge, setting the metals free. Sodium carbonate and borax react upon the acid and basic constituents, respectively, of the charge, and produce slags. Alumina and other oxides either combine with these reagents or dissolve in the slag mixture. There is a copious evolution of gases, such as carbon dioxide, carbon monoxide, sulphur dioxide, and nitrogen. The third stage is known as the period of quiet fusion. It is for the purpose of completing the slag forming reactions and of rendering the slag as liquid as possible. This enables all of the small particles of lead to fall down through the slag, collecting the remaining traces of gold and silver. The latter are washed out of the slag much as a shower of rain sweeps the dust particles out of the air. The slag must be thoroughly liquid in order to insure a perfect separation from the lead.

A high temperature at the beginning of the fusion should be avoided, as it not only increases the chances of boiling over, but may cause some volatilization of compounds of the precious metals. After these metals are reduced and alloyed with lead the temperature can be raised with less danger of loss. A row of empty crucibles or a prism of coke should be placed in front of the crucibles containing the fusions, and the muffle door should be kept closed.

The time required ranges from 40 to 55 minutes, according to conditions. A long continued fusion at a low temperature usually means a small lead button and an imperfect collection of the gold and silver.

The period of quiet fusion should last about 10 to 15 minutes. The crucibles are then taken out of the muffle, tapped gently with a whirling motion, to collect stray shots of lead, and the contents poured into conical iron moulds. The greater part of the slag should be poured off first, so as to avoid splashing of the lead against the sides of the mould. When cold the lead buttons are taken out and hammered into rough cubes, so as to remove the adhering slag. The lead buttons are now ready for cupellation.

**Crucible Charges.** — It is impossible to give a crucible charge that would be satisfactory in every case. Modifications in the amount and kind of reagents must be made to suit the character of the material to be assayed. However, the variations are not so great as is generally supposed, and many assayers use stock fluxes for a great variety of ores and metallurgical products. Changes are made only when the conditions seem to require them.

The following table gives the approximate amount of the different reagents used in an ordinary crucible fusion: —

| | |
|---|---|
| Ore | $\frac{1}{2}$ Assay ton |
| Sodium carbonate | 25 to 35 grams |
| Borax glass | 10 to 15 grams |
| Flour or Nitre | As required. (See Preliminary Assay) |
| Litharge | 60 to 75 grams. |

**The Scorification Assay.** — The scorification assay is used principally in those cases in which an undue amount of interfering base metals would be reduced along with the lead if crucible fusions were made. Thus, if a crucible fusion be made upon an ore containing copper or antimony, either of these two metals will be reduced along with the lead and produce a button which is difficult to cupel. Even with sulphide ores there is a considerable reduction of the copper or antimony, as is shown in the following reactions:

(10) $Cu_2S + 3PbO + Na_2CO_3 = Cu_2 + 3Pb + Na_2SO_4 + CO_2$

(11) $Sb_2S_3 + 9PbO + 3Na_2CO_3 = Sb_2 + 9Pb + 3Na_2SO_4 + 3CO_2$

Nickel and cobalt are reduced in the same way.

In the scorification assay the operations are carried out under oxidizing conditions so as to prevent the reduction of the interfering metals. Metallic lead is used as the collector and is added as such. The flux is mainly litharge, coming from the oxidation of the lead, and a small amount of borax.

The operation is conducted in shallow fire clay dishes known as scorifiers, from 2 to 3 inches in diameter. The amount of ore taken is usually 1–10 assay-ton, sometimes 1–20 or 1–5 assay-ton. About 25 grams of granulated lead are spread over the bottom of the scorifier and the ore then added and thoroughly mixed with the lead. The mixture is then covered with about 25 grams more of granulated

lead and one or two grams of borax glass. Usually from 5 to 20 portions of the ore are weighed up so as to lessen the chances of error. The scorifiers are placed in a muffle heated to redness and the door closed. As soon as the lead melts the door is opened, in order to admit air and increase the rapidity of the oxidation. The ore is seen to be floating on the lead. The latter begins to oxidize and the litharge produced in turn oxidizes the sulphides in the ore, assisted by the oxygen of the air. The temperature at this point must be low in order to prevent volatilization of gold and silver. The ore is not protected by a large bulk of fluxes as it is in the crucible assay. As the oxidation proceeds a ring of slag, mainly litharge, begins to form around the bath of lead. The ore gradually disappears, the gold and silver going into the molten lead and the gangue combining with or dissolving in the litharge. Owing to the strong oxidizing conditions, most of the copper and practically all of the antimony present go into the slag. As the ring of slag increases the temperature is raised. Finally, the lead becomes completely covered, and the muffle door is closed in order that the slag may become thoroughly liquid. The contents of the scorifiers is then poured into conical moulds, as in the case of the crucible fusions. The lead buttons should weigh from 15 to 20 grams. Very small buttons usually mean low results. With high copper material it is sometimes necessary to scorify two or three times and to use a large amount of lead. The buttons are cleaned and cupelled in the usual way.

The scorification assay is not adapted to ores containing volatile constituents, such as tellurides, arsenides and metallic zinc. Carbonates and highly oxidized ores are also unsuited to this method. If the ore contains much basic gangue it should not be scorified, as there is not enough acid flux to take care of it. Low grade gold ores are not usually assayed by scorification because of the small amount of ore taken. In practice the method is limited to ores and metallurgical products containing considerable quantities of antimony, copper, nickel and cobalt. It is a standard method for the assay of copper matte. Scorification is also sometimes used to reduce the size of and to purify lead buttons produced in the crucible method.

**Cupellation.** — Cupellation is the process by which the gold and silver are separated from the lead and other base metals with which they are alloyed. The cupels have already been described. They must be thoroughly dry and somewhat heavier than the lead buttons that are to be cupelled. A bone ash cupel will absorb about its own weight of litharge, but the absorption becomes slower when the saturation point is approached.

In the cupellation process the lead is oxidized to litharge which is taken into the pores of the cupel by capillary attraction. This takes place because litharge is molten at the temperature of the operation. Most of the other base metal oxides are infusible at this temperature. When in moderate amounts, however, they dissolve in the

liquid litharge and are carried into the cupel. If the lead contains much copper and antimony the oxides of these latter metals accumulate on the cupel and may ruin the assay. Hence the need for scorification in these cases.

The cupels should be heated in the muffle for at least 20 minutes before putting in the lead buttons. Cupellations are best started at a bright red heat, say about 900° C. As soon as the buttons are put into the cupels the muffle door should be closed. If the temperature is too low an infusible oxide will form on the lead as soon as the latter is melted and refuse to go into the cupel. The disappearance of this film of oxide on further heating is referred to as the "*opening*" or "*uncovering*" of the lead. Sometimes it is necessary to hasten the opening by means of a burning stick of wood placed immediately over the cupel. This reduces the oxide and at the same time raises the temperature. When all of the cupellations are uncovered the muffle door is opened and the temperature lowered rapidly to the lowest possible point at which the operation can proceed. This must be done because a temperature higher than necessary increases the loss of gold and silver. This loss occurs by absorption into the cupel and by volatilization. If the temperature falls too low the buttons "freeze"; that is, the litharge which melts at 883° C., solidifies on top of the liquid lead, which melts at 327° C., and the operation stops.

At first thought it would seem that a temperature slightly above 883° C. would be the proper one for cupellation. As a matter of fact the temperature of the muffle need not be above 750° C. This is due to the fact that the oxidation of the lead generates a considerable amount of heat, and the buttons are thus hotter than either the muffle or the cupels. A good indication of the right cupellation temperature is the formation of solid flakes of litharge, known as "feathers" upon the inner edge of the cupels. The volatilized litharge strikes the comparatively cool bone ash and sublimes as flake crystals.

The presence of impurities usually increases the loss of gold and silver, and adds to the difficulties of the operation. Copper or nickel in quantity may cause the buttons to freeze even at moderately high temperatures. Antimony causes the formation of a hard, infusible crust of lead antimonate which retains silver and which often splits the top of the cupel.

The surface of the lead in the cupel is convex, owing to the high surface tension of the metal. During cupellation the drops of molten litharge can be seen rolling off of the lead and disappearing into the cupel. The surface tension of the melted litharge is less than the attractive force of the bone ash. In scorification, where the vessel is not porous, the litharge froms a concave surface and climbs up the sides of the scorifier. This explains in part the high gold losses in the cupellation of lead containing gold and tellurium. Some of the gold telluride passes into the cupel just as in the case of litharge. Gold telluride is also more volatile than metallic gold.

As the operation proceeds the lead and other base metals gradually oxidize and disappear. Copper and bismuth are less readily oxidized than lead, and hence tend to remain until most of the lead has gone. The temperature should be raised slightly at this point in order to prevent the buttons from solidifying before the base metals are completely oxidized. Small amounts of these metals usually remain, even in a well conducted cupellation. The melting point of gold and silver being considerably higher than the temperature of the muffle, the buttons solidify soon after the base metals are gone. At the moment of solidification the buttons flash or "blick," owing to the release of the latent heat of fusion. If the buttons are large and consist mainly of silver they may "*sprout*" or "*spit*" on being withdrawn quickly. This is due to dissolved oxygen which escapes when the button solidifies. The sprouting may be prevented by covering the silver button with a hot inverted cupel as soon as the cupellation is finished, and allowing the covered cupel to remain in the muffle for several minutes. This insures a slow cooling of the silver bead. After cooling the buttons are removed from the cupel by means of forceps and the adhering bone ash brushed off. The buttons are then weighed on an assay balance to the nearest one-tenth of a milligram. If a half assay-ton of ore was used the results multiplied by two equal the ounces per ton of combined gold and silver.

Cupellation involves the greatest precious metal losses of all the processes in fire assaying. For that reason it must be conducted with care and skill. The loss in silver ranges from 1 to 2 per cent, even under favorable conditions. If there are large amounts of impurities, or if a very high temperature is used, the silver loss may be several times as great. The gold loss is less than that of silver and should not be more than $\frac{1}{2}$ of 1 per cent. In all cases the percentage losses of gold and silver increase as the amounts in the ore decrease.

**Parting.** — Parting is the separation of gold from silver in an alloy containing these metals, and is effected in fire assaying by means of nitric acid. This acid converts the silver into soluble silver nitrate, but is almost without action upon the gold. In order to part readily the alloy must contain at least three times as much silver as gold. Even at this ratio it is difficult to dissolve all of the silver. In practice, it is better to have a much larger proportion of silver, except in the assay of gold and silver bullion. If the buttons produced in the assay of an ore are known to contain enough gold to render parting difficult or impossible they are subjected to the process known as *inquartation*. The buttons after weighing are wrapped with about 10 times their weight of pure silver foil in 3 to 5 grams of sheet lead and then cupelled. The resulting buttons are flattened and parted in the usual manner.

An important point in parting is the strength of the acid. If a strong acid is used at first the gold in the button is liable to break up into a fine powder which is difficult to manage without loss. By

using a rather weak acid, containing from 10 to 20 per cent of $HNO_3$, the gold has a tendency to coalesce into a coherent mass which can be washed and weighed as one piece. The treatment with weak acid is always followed by one with a stronger acid, in order to remove the last traces of silver. The second acid should be about 1.26 sp.gr., made by diluting the concentrated acid with its own volume of water. In the case of buttons containing a small proportion of gold, the first acid should be very weak, not more than 10 per cent $HNO_3$. With more gold a stronger acid can be used, although the weak acid is usually effective, except when the buttons are very large.

The parting may be done in porcelain capsules or in small glass flasks, known as parting flasks. Only a few cubic centimeters of acid are necessary. This should be heated to boiling and the flattened beads then dropped into it. Solution of the silver begins immediately. At the end of about 20 minutes, or when all visible action has ceased, the weak acid solution is decanted into a white casserole, carefully avoiding the loss of any gold. About 3 cubic centimeters of the stronger acid is now added to each flask or capsule and then heated almost to the boiling point. The heating is continued for at least 10 minutes, when all of the silver should be in solution. The acid is then poured off and the gold washed three times by decantation with chlorine-free water. If capsules are used the water is drained out as completely as possible and the capsules then placed on a hot plate or in front of the muffle for drying. If parting flasks are used a fire clay annealing cup is inverted over the top of each completely filled flask and the flask then quickly reversed, allowing the gold to fall quietly into the annealing cup. After removing the flask by a quick side motion, the water is poured off of the gold and the cup placed on the hot plate. The final process is known as annealing. The capsules or annealing cups are placed in the muffle and heated to low redness for about 5 minutes. The heating causes the brownish-black spongy or fibrous gold to coalesce into a dense flake or bead having the characteristic yellow color of the metal. The annealing also serves to drive off any volatile impurities which may be present, and to render it easier to separate any specks of dust or dirt from the gold. After cooling the gold is weighed on a delicate balance to the nearest .01 milligram — with a little care to the nearest .005 milligram. The weight of the gold is deducted from the weight of the button before parting and the difference represents the silver in the portion taken for assay.

## THE ASSAY OF BULLION

Bullion is an alloy of gold and silver with variable amounts of one or more of the base metals, and is the semi-final product of most non-ferrous metallurgical plants. In lead smelting this product is usually known as base bullion, in copper smelting as blister copper, and in amalgamation and cyanide processes as retort bullion or doré silver. The base metals may include antimony, arsenic, bismuth, cobalt, copper, lead, mercury, nickel and zinc. Small amounts of selenium and tellurium are usually present, as well as traces of the platinum group of metals. In all cases the assay of bullion resolves itself into a problem of the separation of metals from each other, there being practically no non-metallic elements present.

**Bullion Sampling.** — The sampling of bullion involves some difficulties not encountered in the sampling of ores. Most alloys on solidifying segregate to some extent, so that the cooled metal is never uniform in composition. Whenever possible the samples should be taken from the thoroughly stirred molten alloy and then chilled quickly, either by pouring into water or by pouring into small moulds with thick metals sides and bottoms. When there is danger of oxidation this method of course is not entirely satisfactory. In impure bullion there is often a very uneven distribution of the gold and silver, and it is necessary to drill or saw entirely through the bar in order to obtain accurate results. In copper anode plates and other forms of blister copper the plates or bars are drilled in series, so that the combined sample represents a proper percentage of drillings from all parts of each piece. Lead bullion is sometimes sampled in a similar manner, although in this case the bars are usually punched instead of being drilled. The modern tendency is to take melted samples of all metallic products, even in the case of blister copper.

**The Assay of Lead Bullion.** — The assay of lead bullion ordinarily involves only cupellation and parting. The bullion is often impure, however, and it may then be advisable to scorify the weighed portions before cupelling. If the sample contains much copper or antimony it should always be scorified. The precious metal loss in scorification is less than it is in cupellation, especially in the case of an impure bullion requiring a high temperature in order to cupel it.

Lead bullion is usually run in four portions of one half assay-ton each. The four silver buttons are weighed separately and if there is a satisfactory agreement in the weights the average is taken and the result multiplied by two. The buttons are parted in pairs, thus saving time in washing and weighing. Great care should be exercised in the cupellation of lead bullion and in the subsequent parting, as the bullion is a high grade product, and ordinarily no correction is made for losses in the cupel or otherwise.

**The Assay of Copper Bullion.** — Copper bullion may be assayed by the scorification method, but the results are satisfactory only in the case of the gold. The silver obtained is always much too low. Most of the loss can be recovered by assaying the slag and cupels, but this requires additional time and materials.

The best way to determine gold and silver in copper bullion is to use the so-called combination method, in which the copper is first removed by solution in acid. Formerly nitric acid was used for this purpose, but it was found that the results were usually low in gold. There was a tendency for some of the gold to go into solution. The nitric acid method is a convenient way of determining the silver, as the copper dissolves very rapidly in nitric acid, and the precipitation of silver as chloride is very complete.

For the assay of both gold and silver the sulphuric acid-mercuric nitrate method is recommended. One assay-ton of the finely-ground, well mixed copper borings is treated in a large beaker with 30 cc. of water and 10 cc. of a solution of mercuric nitrate containing 25 grams of mercury per liter. The beaker is well shaken so as to amalgamate the copper, and 100 cc. of concentrated sulphuric acid then added. The beaker is covered, placed on a hot plate and heated until all of the copper is dissolved. This will require from one to two hours, according to the temperature and fineness of the sample. The beaker is now removed and the solution is allowed to cool. 100 cc. of cold water are added, the mixture stirred, and then 400 cc. of boiling water added, with further stirring until all copper sulphate has dissolved. A solution of common salt is now added, just sufficient to precipitate all of the silver and mercury. Only a slight excess must be used, as silver chloride is soluble in strong sodium chloride solution. The beaker is replaced on the hot plate and the contents boiled so as to coagulate the silver chloride. The beaker is then removed, the solution diluted to 600 cc. with cold water and allowed to cool. The solution is then filtered through double filter papers, and the beaker and filter washed with hot water. The beaker should be wiped out with a filter paper and this added to the material in the filter. The filter and its contents are now transferred to a $2\frac{1}{2}$ inch glazed scorifier and the filter paper burned off at a low temperature, so as to avoid loss of silver. After the paper is burned off 30 grams of test lead are added and the material scorified until 12 to 15 grams of lead remain. The scorifier is poured and the lead button cupelled at as low a temperature as possible. The gold and silver are parted in the usual way. The results are very accurate.

The object of the mercuric nitrate is to hasten the solution of the copper by forming a galvanic couple. It prevents also the formation of copper sulphide which is insoluble in dilute sulphuric acid.

Assays should be made in duplicate or triplicate.

## THE ASSAY OF GOLD AND SILVER BULLION

In the fire assay of gold and silver bullion a correction must always be made for the metal losses, because of the great value of the bullion and because the refining losses on a commercial scale are considerably less than the losses in assaying. The assays are, therefore, always run with a check or "proof center." The check is an artificial sample made up so as to have as nearly as possible the exact composition of the bullion to be assayed. Two checks and three portions of the bullion, all five of the same weight, are cupelled and parted under exactly the same conditions. The weights of gold and silver found in the bullion samples are then corrected by adding or subtracting the loss or gain experienced by the gold and silver in the checks. In the assay of gold bullion there is sometimes a gain in the weight of the gold, due to the imperfect elimination of the copper. This, however, should be the same in both checks and bullion samples. Results are reported in "fineness" or parts per 1000.

**Silver Bullion or Doré Bullion Assay.**— A sample of about 500 milligrams of the bullion is accurately weighed out on the assay balance. The weight need not be an even 500 milligrams but its exact amount should be recorded. The bullion is wrapped in from 6 to 8 grams of sheet lead and cupelled with the formation of feathers of litharge. The button is covered with a hot cupel to prevent sprouting. The cupel and button are drawn out of the muffle gradually, and the button is then cleaned, flattened and parted in the usual way. To the weight of the silver a loss of from 1 to $1\frac{1}{2}$ per cent is added. The weight of the comparatively small amount of gold can be taken as it is. The weight of the original button, less the sum of the corrected silver weight and the weight of the gold, represents the amount of base metal. This is usually copper, but may be one or more of a number of other metals. The assayer can usually determine what metals are present by the appearance of the bullion and that of the cupel.

Two checks are now prepared by weighing in each case pure gold, pure silver and pure copper or other base metal in the amounts as found in the preliminary assay just described. Three 500 milligram portions of the bullion are also weighed up. The checks and bullion samples are each wrapped in an amount of sheet lead corresponding to that in the following table, taken from Bugbee's "Text-book of Fire Assaying":

**Lead Ratio in Cupellation**

| *Fineness of Au. and Ag.* | *Wt. of Lead* | *Fineness of Au. and Ag.* | *Wt. of Lead* |
|---|---|---|---|
| 950 | 5 grams | 750 | 11 grams |
| 900 | 7 " | 700 | 12 " |
| 850 | 8 " | 650 | 13 " |
| 800 | 10 " | 600 | 15 " |

The table shows that as the base metal, usually copper, increases the amount of lead must be increased.

Cupellation is performed in a single row of cupels, all of the same size. The checks are placed in the second and fourth cupels. The heat should be kept low enough to allow of the formation of feathers of litharge until at the finish, when the temperature must be raised.

The beads are cleaned, weighed, flattened and parted. The amount of gold and silver loss in the checks is determined and the proper correction applied to the weights of gold and silver found in the bullion samples.

If the bullion contains antimony the process must include scorification, which is applied to checks and samples as well. When bismuth, selenium or tellurium is present in quantity the silver must be separated by means of solution in nitric acid and subsequent precipitation as chloride.

**Gold Bullion Assay.** — The assay of gold bullion is in principle the same as that of silver bullion. As the gold is usually in excess of the silver, however, the process involves inquartation, with the use of a stronger first acid than when parting ordinary silver buttons.

**U. S. Mint Method.** — Sample portions of 500 milligrams are taken for assay. A preliminary cupellation is made as in the case of doré bullion. The amount of silver to be added for the final assay is determined by the touchstone method. The cupelled gold and silver button is rubbed on a piece of black jasper and the streak made compared with those made by alloys of known composition. This gives the fineness within 2 per cent, which is close enough. A ratio of silver to gold of 2 to 1 is used in making up the checks. If no copper is present, about 3 or 4 per cent, is added as it facilitates the removal of the last traces of lead in cupellation. The cupelled buttons are flattened by hammering, annealed at a red heat, and then passed through a pair of jeweller's rolls, until they are converted into fillets about $2\frac{1}{2}$ inches long and $\frac{1}{2}$ inch wide. The fillets are again annealed and rolled up into "cornets" or spirals. Sufficient space should be left between the turns to permit of easy contact with the acid. The parting is done by boiling for 10 minutes in nitric acid of 1.28 sp.gr., and then transferring to another vessel containing acid of the same strength and boiling for 10 minutes longer. The cornets are then washed three times with distilled water, dried, annealed and weighed.

The proofs usually show a slight gain in the weight of the gold, so that the correction is made by subtracting the gain from the average weight of the gold found in the sample portions.

The gold after parting should be in one piece and have smooth edges, as otherwise there is danger of loss.

## THE ASSAY OF CYANIDE SOLUTIONS

A number of methods have been devised for the determination of gold and silver in cyanide solutions. Only two of these methods will be described here.

**Evaporation in Lead Tray.** — This method is adapted to cyanide solutions containing only small amounts of base metals or other impurities. A small tray or boat is made of lead foil, capable of holding the amount of solution to be assayed. A wooden block or form is used to make the trays if many assays are required. The solution has about the same specific gravity as water, so that 29.2 cc. are assumed to be equal to an assay-ton. An amount of solution varying with its richness is put into the lead tray and slowly evaporated to dryness on the hot plate. The lead tray is then folded up and cupelled in the usual manner.

**The Chiddey Method.** — This method, first described by Alfred Chiddey, is adapted to almost every grade and character of cyanide solutions.

From 1 to 20 assay-tons of solution are heated in a beaker or evaporating dish. To the solution is added from 10 to 20 cc. of a 10 per cent solution of lead acetate containing 40 cc. of acetic acid per liter. From $\frac{1}{2}$ to 2 grams of zinc dust or zinc shavings is then added. The gold, silver and lead immediately begin to precipitate on the zinc. The solution is heated for about 20 to 25 minutes, but not to boiling. The lead should coalesce into a spongy mass. Boiling the solution is liable to break up the sponge. The excess zinc is now dissolved by adding slowly 20 cc. of hydrochloric acid of 1.12 sp.gr. The heating is continued until effervescence ceases. It may be necessary to stir slightly in order to make sure that all zinc is dissolved. The solution is now decanted off and the lead sponge washed two or three times with water. The excess water is squeezed out of the sponge with the fingers, the sponge further dried by pressing between filter paper and then rolled into a ball with lead foil and the necessary silver for parting. A hole should be left in the lead foil for the escape of steam. The ball is then dried and cupelled.

As the lead sponge begins to break up and go into solution as soon as all of the zinc is dissolved no time should be lost in decanting the solution after the zinc has disappeared.

**Special Methods of Assay.** — There are many ores and metallurgical products that require special methods for the determination of the gold and silver that they contain. It is impossible to refer to these methods here. A knowledge of the composition of the sample, however, will usually enable the skilled assayer to so modify the ordinary processes as to obtain satisfactory results.

For further details in regard to standard and special methods of fire assaying the reader is referred to such works as "A Manual of Fire Assaying," by Chas. H. Fulton, published in 1911, and "A Textbook of Fire Assaying," by Edward E. Bugbee, published in 1922.

## METHODS FOR ANALYSIS OF COAL

Such tremendous value attaches in boiler-room economy to the character of the fuel that the purchase of coal upon the results of laboratory analysis has grown in importance. Specifications have been drawn with such exact requirements that fairness to the coal contractor requires that only exact methods of analysis be employed.

### SAMPLING

In order that the laboratory sample shall be representative of the delivery, great care must be taken, however; the personal element should be eliminated as far as possible. When possible, coal should be delivered by chutes and a shovelful taken at regular intervals throughout the delivery. If delivered in wagons a portion should be taken from each wagon load. Boat loads are best sampled while being loaded or unloaded. If a pile of coal must be sampled, portions should be taken from all sides, top and bottom. The gross sample should preferably be 200 pounds for deliveries up to 100 tons and one-tenth of 1% of the amount delivered for quantities over 100 tons. Larger sizes should be crushed to at least pea size (about $\frac{3}{4}$ in.) and preferably under. The gross sample should be thoroughly mixed with a shovel, piled up, and quartered. Opposite quarters should then be mixed, piled up and quartered again and this continued until a sample of about 5 pounds is obtained. This sample should then be forwarded to the laboratory in a sealed moisture-tight container. The most satisfactory container is one made of galvanized iron, to prevent rusting, cylindrical in shape with screw cap flush with the sides. A convenient size is 6 in. in diameter by 8 in. in height. Such a can is readily cleaned and sealed. Sealing is conveniently made by pasting a strip of paper around the can over the joint, or by means of wax and an impression seal.

### PREPARATION OF SAMPLE FOR ANALYSIS

The laboratory sample should first receive a number which should follow the sample through all phases of preparation in order to avoid confusion. The whole sample, when received at the laboratory, should be crushed to 4 mesh size or less. The Chipmunk Jaw Crusher is rapid and easily cleaned, as one jaw is removable. If too wet to crush, causing clogging of the crusher, the whole sample should be dried on the steam bath, the moisture so lost determined and added

to the analytical moisture later determined on the pulverized sample. Shallow agateware pans large enough to take the complete sample are convenient and should set in large holes on the steam bath, so that the body of the pan is exposed to the steam and drying is hastened. A few hours only are necessary. The U. S. Bureau of Mines dries in a special oven with a current of dried air at 30–35° C., but this occasions a delay of twelve to ninety-six hours. The

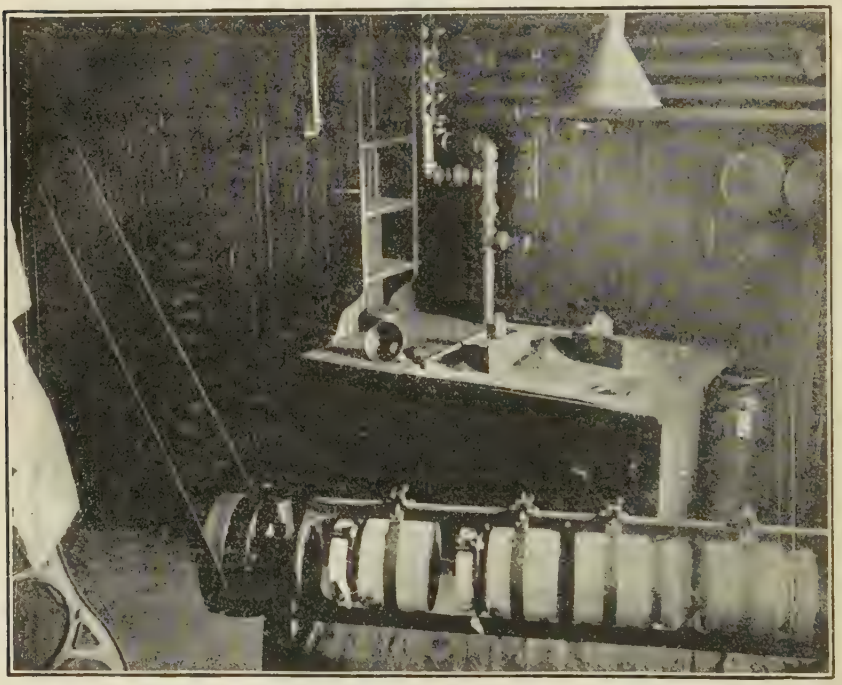


Fig. 132. —Illustrates Method of Quartering Coal. Ball Mill for Pulverizing, and Suction Ventilator.

crushed sample should be mixed and quartered, preferably by hand. This is best and most rapidly done in the old-fashioned way by raising alternately the corners of a large piece of oilcloth or rubber sheet. The pile may be quickly quartered by two V-shaped pieces of galvanized iron to cut and pull away opposite quarters. The remaining quarters should be again mixed and quartered in the same way and the process continued until a 100 gram representative portion is obtained. The discarded quarters should be returned to the can to be retained in case a record analysis is desired. Such check analysis

should always be made upon a freshly quartered and pulverized sample of the remaining portions of the original gross laboratory sample.

The 100 gram sample should then be pulverized in an Abbé Ball Mill for three-quarters of an hour. The jar should be nearly full to produce the most rapid pulverization, that is, contain the full charge of pebbles, about 10 pounds for the 9 in. jar. The speed of revolution should be 60 per minute. Natural flint pebbles are least abraded and produce no appreciable effect upon the ash. The ball mill has two distinct advantages. It conserves the moisture of the coal and it pulverizes so fine that the coal will usually all pass a 60 mesh screen and a large part the 100 mesh screen. This greater fineness prevents incomplete combustion of anthracite coal in the bomb determination to be described later. The pebbles and coal should then be dumped on a covered ash-sifter resting on the oilcloth or rubber sheet, shaken quickly and pebbles and sifter brushed clean. The sample should then be passed through the 60 mesh screen and brushed at once into a moisture tight container. Any material retained on the 60 mesh screen, which occasionally happens, should be quickly pulverized in a small steel mortar. One-half pint, glass-covered lightning jars are convenient for containers.

As the dust in coal sampling is so fine as to penetrate through the clothing to the skin, it is wise to use an aspirator to protect the lungs and also use a suction ventilator to keep the air fresh and clean. The suction should connect with small hoods over the crusher and over the quartering table.

## METHODS OF ANALYSIS

**Moisture.** — Moisture may be accurately determined on a 10-gram sample heated for one hour at 105° C. Close checks will be obtained and weighing is rapid, as the weight need only be taken to the nearest milligram. Glass evaporating dishes of $2\frac{3}{4}$ in. diameter are convenient for this determination. The Beans electric thermo-regulator for gas has been found very satisfactory for oven regulation, as the oven may be heated rapidly and will quickly come to adjustment. The Freas oven is an excellent electric type.

Most laboratories employ a 1-gram sample, however, and later use the residue for ash determination. The Bureau of Mines uses a

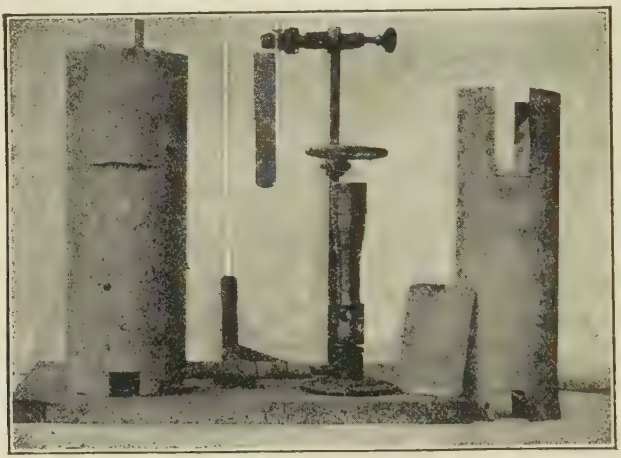


Fig. 133. — V. C. M. Apparatus

special drying oven and a specially prepared sample for moisture. The 4 mesh sample is crushed in a roll or coffee-mill crusher to 20-mesh, and bottled quickly without sieving.

**Ash.** — The ash represents the mineral matter in coal after ignition. No attempt is made in common practice to calculate the original form of the constituents. It is best determined upon a separate portion of coal, and preferably in silica crucibles, as the wear on platinum is considerable. Heating should be slow and careful at first, to avoid loss from volatile matter and to avoid the effect of coking. Later the contents should be stirred with a platinum wire to facilitate combustion, not neglecting to tap the wire free from ash. The silica crucibles should rest on silica or nichrome triangles.

Some laboratories employ a muffle furnace and others an electric furnace.

The residue from moisture may be used for ash determination, but the residue from volatile combustible matter should not be so used, as there is danger of mechanical loss of ash in the rapid heating, and the accuracy of the ash-figure is far more important than the volatile combustible matter.

A 1 gram sample is used for the ash determination.

**Volatile Combustible Matter.** — This determination is entirely empirical and should be performed under strictly standard conditions. The determination is made upon a 1 gram sample heated for seven minutes, timed by a stopwatch, in a platinum crucible of 25–30 cc. capacity, and with tight-fitting cover. The crucible and cover should be kept brightly polished. A special apparatus should be arranged. Construct a cylinder of asbestos or galvanized iron to protect the flame and crucible. Connect an adjustable Meeker burner (Scimatco type is preferable) with a U-tube to measure the gas pressure. Arrange a platinum wire from a triangle to support the bottom of the crucible always at the same distance from the burner.

Calibrate the apparatus by adjusting the burner and pressure so that the crucible is entirely surrounded by the flame and the temperature is about 950° C. This may be determined most conveniently by the fusing-point of potassium chromate. Note the gas pressure required and in the analysis set the gas at this pressure. In this way close checks may conveniently be obtained when the right conditions have been determined.

The loss in weight minus the moisture is the volatile combustible matter.

A 10–20 cc. crucible has recently been advocated to reduce the effect of oxidation by oxygen in the crucible. Several different schemes have been advocated in order to obtain uniform results. An electric furnace is used by some. Any method is empirical, as the determination does not represent any very definite constituent of the coal. Originally intended as a measure of coking ability the V.C.M. is now mainly a means of discriminating between different kinds of coal and as a means of keeping within the smoke ordinances.

**Volatile Sulphur.** — The total sulphur in a coal is of little importance. If desired, it may be determined by the well-known Eschka method. The volatile sulphur is of great importance both in its bearing upon fusibility by indicating the presence of pyrites in the coal and in its relation to corrosion by the formation of sulphurous acid.

Volatile sulphur is determined in the bomb washings after a calorific determination. These washings are filtered if necessary and titrated for acidity for one of the corrections in the calorific calculation. The sulphur is then determined most rapidly and conveniently by a Jackson Candle Turbidimeter.

"The titrated solution is made up to 200 cc. The amount of acidity found is used as a guide in selecting the aliquot for the sulphur determination. In the case of anthracite coals, the amount taken is one-fourth to one-half; in the case of soft coals from one-fourth to one-tenth of the whole."

TURBIDIMETRIC SULPHUR TABLE

For use with Jackson's candle turbidimeter

Sulphur and $SO_3$ contained in 100 cc. precipitated

| Depth. Cm. | S. Mg. | $SO_3$. Mg. | Depth. Cm. | S. Mg. | $SO_3$. Mg. | Depth. Cm. | S. Mg. | $SO_3$. Mg. |
|---|---|---|---|---|---|---|---|---|
| 1.0 | 20.0 | 50.0 | 5.0 | 3.66 | 9.15 | 9.0 | 2.30 | 5.75 |
| 1.1 | 18.0 | 45.0 | 5.1 | 3.60 | 9.00 | 9.1 | 2.28 | 5.70 |
| 1.2 | 16.5 | 41.3 | 5.2 | 3.54 | 8.85 | 9.2 | 2.26 | 5.65 |
| 1.3 | 15.0 | 37.5 | 5.3 | 3.49 | 8.73 | 9.3 | 2.25 | 5.63 |
| 1.4 | 13.5 | 33.8 | 5.4 | 3.43 | 8.58 | 9.4 | 2.23 | 5.58 |
| 1.5 | 12.5 | 31.3 | 5.5 | 3.38 | 8.45 | 9.5 | 2.21 | 5.53 |
| 1.6 | 11.2 | 28.0 | 5.6 | 3.33 | 8.33 | 9.6 | 2.19 | 5.48 |
| 1.7 | 10.0 | 25.0 | 5.7 | 3.28 | 8.20 | 9.7 | 2.18 | 5.45 |
| 1.8 | 9.5 | 23.8 | 5.8 | 3.24 | 8.10 | 9.8 | 2.16 | 5.40 |
| 1.9 | 9.0 | 22.5 | 5.9 | 3.20 | 8.00 | 9.9 | 2.15 | 5.38 |
| 2.0 | 8.5 | 21.3 | 6.0 | 3.15 | 7.88 | 10.0 | 2.13 | 5.33 |
| 2.1 | 8.0 | 20.0 | 6.1 | 3.11 | 7.78 | 10.1 | 2.11 | 5.28 |
| 2.2 | 7.6 | 19.0 | 6.2 | 3.07 | 7.68 | 10.2 | 2.10 | 5.25 |
| 2.3 | 7.3 | 18.3 | 6.3 | 3.03 | 7.58 | 10.3 | 2.09 | 5.23 |
| 2.4 | 7.0 | 17.5 | 6.4 | 2.99 | 7.48 | 10.4 | 2.07 | 5.18 |
| 2.5 | 6.7 | 16.8 | 6.5 | 2.95 | 7.38 | 10.5 | 2.06 | 5.15 |
| 2.6 | 6.5 | 16.3 | 6.6 | 2.92 | 7.30 | 10.6 | 2.04 | 5.10 |
| 2.7 | 6.3 | 15.8 | 6.7 | 2.88 | 7.20 | 10.7 | 2.03 | 5.08 |
| 2.8 | 6.1 | 15.3 | 6.8 | 2.85 | 7.13 | 10.8 | 2.02 | 5.05 |
| 2.9 | 5.9 | 14.8 | 6.9 | 2.82 | 7.05 | 10.9 | 2.01 | 5.03 |
| 3.0 | 5.7 | 14.3 | 7.0 | 2.79 | 6.98 | 11.0 | 2.00 | 5.00 |
| 3.1 | 5.5 | 13.8 | 7.1 | 2.76 | 6.90 | 11.1 | 1.98 | 4.95 |
| 3.2 | 5.4 | 13.5 | 7.2 | 2.73 | 6.83 | 11.2 | 1.97 | 4.93 |
| 3.3 | 5.2 | 13.0 | 7.3 | 2.70 | 6.75 | 11.3 | 1.95 | 4.88 |
| 3.4 | 5.1 | 12.8 | 7.4 | 2.67 | 6.68 | 11.4 | 1.94 | 4.85 |
| 3.5 | 5.0 | 12.5 | 7.5 | 2.64 | 6.60 | 11.5 | 1.93 | 4.83 |
| 3.6 | 4.85 | 12.25 | 7.6 | 2.61 | 6.53 | 11.6 | 1.92 | 4.80 |
| 3.7 | 4.75 | 12.00 | 7.7 | 2.59 | 6.48 | 11.7 | 1.91 | 4.78 |
| 3.8 | 4.63 | 11.75 | 7.8 | 2.56 | 6.40 | 11.8 | 1.90 | 4.75 |
| 3.9 | 4.52 | 11.50 | 7.9 | 2.54 | 6.35 | 11.9 | 1.89 | 4.73 |
| 4.0 | 4.43 | 11.25 | 8.0 | 2.51 | 6.28 | 12.0 | 1.88 | 4.70 |
| 4.1 | 4.33 | 11.00 | 8.1 | 2.49 | 6.23 | 12.1 | 1.87 | 4.68 |
| 4.2 | 4.24 | 10.75 | 8.2 | 2.47 | 6.18 | 12.2 | 1.86 | 4.65 |
| 4.3 | 4.16 | 10.50 | 8.3 | 2.44 | 6.10 | 12.3 | 1.85 | 4.63 |
| 4.4 | 4.08 | 10.25 | 8.4 | 2.42 | 6.05 | 12.4 | 1.84 | 4.60 |
| 4.5 | 4.00 | 10.00 | 8.5 | 2.40 | 6.00 | 12.5 | 1.83 | 4.58 |
| 4.6 | 3.93 | 9.83 | 8.6 | 2.38 | 5.95 | 12.6 | 1.82 | 4.55 |
| 4.7 | 3.86 | 9.65 | 8.7 | 2.36 | 5.90 | 12.7 | 1.81 | 4.53 |
| 4.8 | 3.79 | 9.48 | 8.8 | 2.34 | 5.85 | 12.8 | 1.80 | 4.50 |
| 4.9 | 3.72 | 9.30 | 8.9 | 2.32 | 5.80 | 12.9 | 1.79 | 4.48 |

TURBIDIMETRIC SULPHUR TABLE.—*Continued*

| Depth. Cm. | S. Mg. | $SO_3$. Mg. | Depth. Cm. | S. Mg. | $SO_3$. Mg. | Depth. Cm. | S. Mg. | $SO_3$. Mg. |
|---|---|---|---|---|---|---|---|---|
| 13.0 | 1.78 | 4.45 | 17.1 | 1.49 | 3.73 | 21.1 | 1.24 | 3.10 |
| 13.1 | 1.77 | 4.43 | 17.2 | 1.49 | 3.73 | 21.2 | 1.23 | 3.08 |
| 13.2 | 1.76 | 4.40 | 17.3 | 1.48 | 3.70 | 21.3 | 1.23 | 3.08 |
| 13.3 | 1.75 | 4.38 | 17.4 | 1.47 | 3.68 | 21.4 | 1.22 | 3.05 |
| 13.4 | 1.74 | 4.35 | 17.5 | 1.47 | 3.68 | 21.5 | 1.21 | 3.03 |
| 13.5 | 1.73 | 4.33 | 17.6 | 1.46 | 3.65 | 21.6 | 1.21 | 3.03 |
| 13.6 | 1.73 | 4.33 | 17.7 | 1.45 | 3.63 | 21.7 | 1.20 | 3.00 |
| 13.7 | 1.72 | 4.30 | 17.8 | 1.44 | 3.60 | 21.8 | 1.20 | 3.00 |
| 13.8 | 1.71 | 4.28 | 17.9 | 1.44 | 3.60 | 21.9 | 1.19 | 2.98 |
| 13.9 | 1.70 | 4.25 | 18.0 | 1.43 | 3.58 | 22.0 | 1.18 | 2.95 |
| 14.0 | 1.70 | 4.25 | 18.1 | 1.43 | 3.58 | 22.1 | 1.18 | 2.95 |
| 14.1 | 1.69 | 4.23 | 18.2 | 1.42 | 3.55 | 22.2 | 1.17 | 2.93 |
| 14.2 | 1.68 | 4.20 | 18.3 | 1.41 | 3.53 | 22.3 | 1.16 | 2.90 |
| 14.3 | 1.67 | 4.18 | 18.4 | 1.41 | 3.53 | 22.4 | 1.16 | 2.90 |
| 14.4 | 1.66 | 4.15 | 18.5 | 1.40 | 3.50 | 22.5 | 1.15 | 2.88 |
| 14.5 | 1.66 | 4.15 | 18.6 | 1.40 | 3.50 | 22.6 | 1.15 | 2.88 |
| 14.6 | 1.65 | 4.13 | 18.7 | 1.39 | 3.48 | 22.7 | 1.14 | 2.85 |
| 14.7 | 1.64 | 4.10 | 18.8 | 1.38 | 3.45 | 22.8 | 1.13 | 2.83 |
| 14.8 | 1.63 | 4.08 | 18.9 | 1.38 | 3.45 | 22.9 | 1.13 | 2.83 |
| 14.9 | 1.62 | 4.05 | 19.0 | 1.37 | 3.43 | 23.0 | 1.12 | 2.80 |
| 15.0 | 1.62 | 4.05 | 19.1 | 1.37 | 3.43 | 23.1 | 1.11 | 2.78 |
| 15.1 | 1.61 | 4.03 | 19.2 | 1.36 | 3.40 | 23.2 | 1.11 | 2.78 |
| 15.2 | 1.60 | 4.00 | 19.3 | 1.35 | 3.38 | 23.3 | 1.10 | 2.75 |
| 15.3 | 1.60 | 4.00 | 19.4 | 1.35 | 3.38 | 23.4 | 1.09 | 2.73 |
| 15.4 | 1.59 | 3.98 | 19.5 | 1.34 | 3.35 | 23.5 | 1.08 | 2.70 |
| 15.5 | 1.59 | 3.98 | 19.6 | 1.34 | 3.35 | 23.6 | 1.08 | 2.70 |
| 15.6 | 1.58 | 3.95 | 19.7 | 1.33 | 3.33 | 23.7 | 1.07 | 2.68 |
| 15.7 | 1.57 | 3.93 | 19.8 | 1.32 | 3.30 | 23.8 | 1.06 | 2.65 |
| 15.8 | 1.57 | 3.93 | 19.9 | 1.32 | 3.30 | 23.9 | 1.05 | 2.63 |
| 15.9 | 1.56 | 3.90 | 20.0 | 1.31 | 3.28 | 24.0 | 1.05 | 2.63 |
| 16.0 | 1.56 | 3.90 | 20.1 | 1.30 | 3.25 | 24.1 | 1.04 | 2.60 |
| 16.1 | 1.55 | 3.88 | 20.2 | 1.30 | 3.25 | 24.2 | 1.03 | 2.58 |
| 16.2 | 1.54 | 3.85 | 20.3 | 1.29 | 3.23 | 24.3 | 1.03 | 2.58 |
| 16.3 | 1.54 | 3.85 | 20.4 | 1.28 | 3.20 | 24.4 | 1.02 | 2.55 |
| 16.4 | 1.53 | 3.83 | 20.5 | 1.28 | 3.20 | 24.5 | 1.02 | 2.55 |
| 16.5 | 1.53 | 3.83 | 20.6 | 1.27 | 3.18 | 24.6 | 1.01 | 2.53 |
| 16.6 | 1.52 | 3.80 | 20.7 | 1.26 | 3.15 | 24.7 | 1.01 | 2.53 |
| 16.7 | 1.52 | 3.80 | 20.8 | 1.26 | 3.15 | 24.8 | 1.00 | 2.50 |
| 16.8 | 1.51 | 3.78 | 20.9 | 1.25 | 3.13 | 24.9 | 1.00 | 2.50 |
| 16.9 | 1.50 | 3.75 | 21.0 | 1.25 | 3.13 | 25.0 | 1.00 | 2.50 |
| 17.0 | 1.50 | 3.75 | | | | | | |

"The aliquot of the solution to be tested is measured into the turbidimeter tube, diluted to near the 100 cc. mark, shaken, then acidified with 1 cc. of (1 : 1) hydrochloric acid, made up to the mark, and mixed well by shaking. A barium chloride tablet weighing

1 gram[1] and compressed without the use of a binder is then dropped in and the tube closed by means of a clean rubber stopper. The tube is then tilted up and down, causing the tablet to roll back and forth through the solution by gravity.

"When the precipitation appears to be complete, the remainder of the tablet may be dissolved by rapidly rotating the tube; but violent shaking should be avoided, since it would have a tendency to cause aggregation of the precipitate. The turbid liquid is then transferred to a beaker, the candle lighted, a small quantity of the liquid poured into the glass tube to prevent overheating and cracking, and the tube put in place. More of the liquid is then poured in, allowing it to run down the side of the tube, rapidly at first, until the image of the flame becomes dim, then more slowly, waiting a moment after each addition until the liquid in the tube is quiet, and continuing thus until the *image* of the flame just disappears. The depth of the liquid in centimeters is noted. The mixture is then returned to the beaker, poured back and forth from beaker to tube two or three times, and read again as before.

"The precipitated solution is read at least twice, and the readings usually check exactly, unless they fall in the upper part of the tube where they may differ by a centimeter without materially altering the results. In this case readings may be averaged. The amount of sulphur corresponding to the depth of liquid in the tube is found in the table, and multiplied by the proper factor, depending on the aliquot of the original solution taken.

"All dilutions must be made before precipitation, for otherwise the results will not be concordant for different dilutions. The average time required is ten minutes or less. The method carried out as described is accurate to about 0.05% sulphur."

**Fixed Carbon.** — Fixed carbon is found by adding the moisture, ash, and volatile matter together, and subtracting from 100%.

**Calorific Value.** — Heat value is expressed as "small calorie (cal.)," the amount of heat required to raise the temperature of 1 gram of water 1° C., "large calorie (Cal.)," the amount of heat required to raise the temperature of 1 kilogram of water 1° C., and "British thermal unit (B.t.u.)," the amount of heat required to raise the temperature of 1 pound of water 1° F., at or near 39.1° F. Small calories per gram of coal multiplied by 1.8 equal B.t.u. per pound of coal.

It is preferable to express results as B.t.u. per pound of dry coal, instead of coal as received, since comparison between different samples of coal and the results of different analysts and laboratories are

[1] On standing for some time, some of the tablets become coated with a thin layer of effloresced salt. This should be removed by gently rubbing between the fingers before using the tablet. It is not advisable to keep the tablets in a moist atmosphere to prevent this efflorescence, as they become extremely hard and difficult to dissolve.

facilitated. The other determinations except moisture are also better expressed on the dry basis.

As a check upon accuracy of work and to catch errors, results of B.t.u. should also be calculated to B.t.u. per pound of combustible, that is, divide the B.t.u. dry basis by (100% minus the per cent of ash). For the same run of coal, this value changes but little, usually within 200 B.t.u.

The calorific determination should be made by means of a bomb calorimeter. The platinum-lined Atwater type is convenient. The Emerson is more commonly used in this country. Fig. 134.

One gram of the 60-mesh sample of coal prepared for analysis is weighed into a nickel capsule (28 mm. top width, 23 mm. bottom

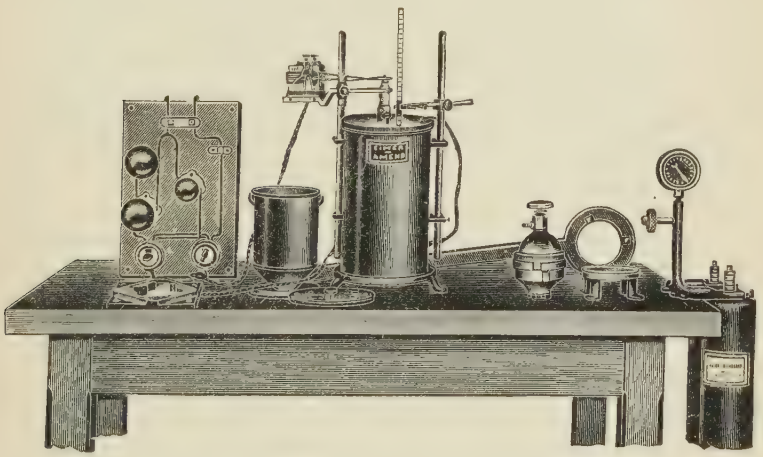


Fig. 134. Emerson Calorimeter and Accessories.

width, and 12 mm. depth) in the bottom of which has been placed an ignited disc of asbestos paper. The latter prevents incomplete combustion of anthracite coal by preventing chilling of the coal after combustion starts. In weighing large numbers of samples a piece of tared platinum foil is convenient and the coal transferred with a camel's-hair brush into the nickel capsule. The capsule is supported on a platinum ring suspended by a platinum wire from the head of the bomb. A piece of iron fuse wire, No. 34 B. &. S. gauge, and weighing 10 milligrams, is attached at one end to the wire supporting the tray and at the other end to another platinum wire extending downward from the head, but insulated from it. Attachment of the fuse wire is made by winding around the platinum wires several times. The center of the fuse wire should dip into the coal slightly. A convenient method of obtaining pieces of fuse wire of

uniform weight is to wind around a flat piece of board or cardboard and cut the loops.

The shell of the bomb is rinsed with water and sufficient moisture, one-half cc., is thus left to take up the acids formed by combustion. The head is next joined gas tight to the shell of the bomb by the collar. Lead gaskets render these joints tight. Oxygen gas is slowly introduced, so as not to blow the coal out of the pan, until about 21 atmospheres pressure is recorded in the bomb. The needle valve is then closed just tight enough to prevent leakage, the valve on the oxygen tank closed and the bomb disconnected. Twenty atmospheres pressure should remain in the bomb for the combustion, an amount sufficient for complete combustion of the coal and an amount containing sufficient nitrogen together with the nitrogen in the air trapped in the bomb to cause the sulphur to burn to sulphuric acid completely, unless the sulphur is unusually high.

The bucket is filled with enough distilled water, about 3° C. below the room temperature, to make the water equivalent of the calorimeter some round number, i.e., 2000 g. with Atwater, 2900 g. with Mahler, or 2350 g. with Emerson. The water is best weighed on a balance, capable of delicacy with such heavy weights, and the amount of water should be sufficient to cover the bomb. The bomb is placed in its support and placed in the water in the bucket. The latter is set in the calorimeter, the stirrer added so as not to touch the bomb or bucket, covers applied and thermometer placed in the water and adjusted so that it can be read during the combustion. The thermometers should be special and standardized by the Bureau of Standards. The Fuess type of Beckmann is excellent.

Connect the poles of six dry cells to the stem and insulated post of the bomb. Connection should be made with a button for firing the coal. It is also convenient to have a small electric lamp connected with the button to indicate that the batteries are in condition, before a run is started.

The calorific determination should be made in a room protected from sudden changes of temperature and from draughts. If a current of air strikes the thermometer during a determination, the results will be untrustworthy. Mechanical stirring is preferable and should be at a moderate rate. The stirrer is started and after a couple of minutes or so, when conditions have become uniform, the thermometer is read by means of a telescope and readings taken every one-half minute for six readings. Interpolate to the 0.001° C. A clock striking every half minute is convenient. After the sixth reading, fire the coal by pressing the button connected with the batteries and take approximate readings of the thermometer every half minute, reading to the 0.001° C. as soon as the rise is slow enough to do so. After the maximum temperature has been reached, take six more readings at half-minute intervals.

Remove the bomb from the bucket and allow the gas to escape slowly. Disconnect the head and rinse out the bomb thoroughly. Titrate the washings with N/10 sodium carbonate, using methyl orange as indicator. Determine the sulphur, after titration, with the turbidimeter as under Volatile Sulphur.

**Calculation of B.t.u.** — The table on page 730 is an example of an actual determination, showing corrections as applied.

Corrections must be applied to the thermometer in accordance with the certificate furnished for each thermometer by the Bureau of Standards, including the correction for temperature of setting of Beckman thermometers and emergent stem correction for others.

The thermometer should also be fitted with a vibrator to overcome meniscus error. This is conveniently done by arranging a small electric vibrator so that the hammer hits the rubber-covered metal clamp supporting the thermometer. The vibrator should, of course, be connected to a push-button and dry batteries.

Correction must also be made for changes of temperature due to radiation. A simple formula which yields results within 0.002° C. as compared with the more elaborate formulas is the following:

$$\frac{x(a+b)}{2} + yb = \text{radiation correction.}$$

$a$ = average preliminary period change per half minute;
$b$ = average final period change per half minute;
$x$ = number of half-minute intervals of combustion period during each of which the rise of temperature (expressed to the nearest 0.01° C.) was greater than 10% of the total rise. This is readily seen by inspection;
$y$ = remaining number of half-minute intervals of combustion period.

The algebraic signs must be observed in the formula.

The end of the combustion period is taken as the first reading after the maximum temperature. The reason for this rests in the fact that the real maximum rarely occurs at a half-minute interval reading, as shown by a drop during the first period after the maximum temperature read, of less than the average final change. Correcting for an extra combustion interval counteracts this error.

The nitrogen in the coal and in the air of the bomb forms nitric acid. This does not occur when coal is burned in the furnace, hence the bomb determination is too high by the amount of heat thus produced. The calorific value of nitrogen burning to nitric acid is 230 calories per gram of nitric acid. Each cubic centimeter of N/10 sodium carbonate used in the titration represents 1.45 calories.

Furthermore, sulphur in the furnace burns to the dioxide and in the bomb to the trioxide. This excess heat in the bomb must be deducted. Again, it should be remembered that all of the above acidity is not nitric but is partly sulphuric acid. This correction is conveniently

made by adding to the acidity correction (made as if it were all nitric acid) 13 calories for each 0.01 gram of sulphur. This represents the excess which the oxidation correction is over its expression as the formation of nitric acid as obtained from the titration.

The correction for the iron fuse wire is 16 calories for each 10 milligrams.

## NO. 1 BUCKWHEAT COAL

Thermometer used ($T_5$), zero set at 20.4° C.

Room Temperature 22.5° C. Atwater bomb.

| | | |
|---|---|---|
| Acid found equal 7.2 cc. of N/10 $Na_2CO_3$ × 1.45 cal. | = 10.4 | calories |
| Volatile sulphur (aliquot ½) 8.6 cm. = .0048 gram × 13 cal. | = 6.2 | calories. |
| Iron wire (10 milligrams) | = 16.0 | calories |
| | 32.6 | calories |

Thermometer readings, Half minute intervals

| | |
|---|---|
| Preliminary period | 0.979 |
| | 0.980 |
| | 0.980 |
| | 0.981 |
| | 0.983 |
| | 0.984 |
| | 0.986 |

Average rise in temperature:

$$\frac{.007}{5} = .0014$$

| | |
|---|---|
| Combustion period | 1.600 |
| | 3.270 |
| | 4.050 |
| | 4.225 |
| | 4.267 |
| | 4.278 |
| | 4.279 |
| | 4.278 |

| | |
|---|---|
| Final period | 4.273 |
| | 4.270 |
| | 4.268 |
| | 4.264 |
| | 4.260 |

Average fall in temperature:

$$\frac{.018}{5} = .0036$$

| | |
|---|---|
| Corrected temperature, end of combustion period | 4.277 |
| Corrected temperature, end of preliminary period | 0.986 |
| Apparent rise in temperature corrected for thermometer calibration | 3.291 |
| Thermometer correction for setting and room temperature | + 0.022 |
| Apparent rise in temperature, corrected for thermometer setting | 3.313 |
| Radiation correction: $3\left(\frac{(-.0014)+(+.0036)}{2}\right)+5(+.0036)$ | + 0.021 |
| Corrected rise in temperature | 3.334 |
| Water equivalent (grams) | 2000 |
| Calories (2000 × 3.334) | 6668.0 |
| Correction for acidity, sulphur trioxide and iron | 32.6 |
| Actual calories, coal as received | 6635.4 |
| Calories (dry basis) 6635.4 ÷ .9522 (100% − moisture) | 6968.5 |
| B.t.u. per lb. of coal (dry basis) (6968.5 × 1.8) | 12,543 |
| B.t.u. per lb. of combustible (dry basis) 12,543 ÷ .842 (100% − ash) | 14,897 |

| | |
|---|---|
| B.T.U | 12,543 |
| V.C.M | 7.7 % |
| Ash | 15.8 % |
| Vol. sulphur | 0.48 % |
| Moisture | 4.78 % |

All other corrections are met by standardization under conditions similar to those under which the calorimeter is to be used. Such errors arise from loss of heat by evaporation of water while stirring (probably covered by the radiation correction), gain in heat due to combustible gases in the oxygen, changes in specific heat of water at various temperatures, changes in the gases present after combustion, and changes of pressure of the gases in the bomb. The last three errors are too small to take into account. The oxygen error has disappeared since the introduction of the purer gas manufactured by the Linde Air Products Company.

Inspection of the bomb contents should always be made to insure that there are no sooty deposits or coal thrown from the capsule. Some coals require to be compressed into pellets to prevent the above.

The procedure outlined above, using half-minute intervals, saves considerable time (nearly one-half) over the usual procedure and produces very accurate results.

**Standardization of the Calorimeter.** — While there are several ways of determining the water equivalent of the calorimeter, that is, the heat capacity of the apparatus expressed as though it were all water, only one method should be used by commercial laboratories, and that is to burn in the calorimeter a known weight of pure substance, the calorific value of which has been determined by the Bureau of Standards, Washington, D. C. Of those furnished, benzoic acid is preferable, as it readily ignites and burns completely. If cane sugar should be used, a few milligrams of benzoic acid are necessary to assist ignition and correction must be made for its heating value. Cane sugar does not always burn completely.

Procure standardized benzoic acid from the Bureau of Standards. Compress into pellets by means of a pellet press sufficient benzoic acid to produce approximately as many calories as are given by the coal, that is, about 7000 calories. One gram of benzoic acid produces 6320 calories. Determine in the calorimeter the temperature rise produced by the benzoic acid with the precautions used in a regular coal analysis, correcting for thermometer and radiation errors. Multiply the grams of benzoic acid taken by 6320 calories, add the calories produced by formation of nitric acid as obtained from the titration and add the calories produced by the iron fuse wire. Divide this sum by the corrected rise in temperature. The quotient is the water-equivalent of the calorimeter. The amount of water added to the bucket is then changed so as to make the total calorimeter equivalent a round number, such as 2000 for the Atwater or 2900 for the Mahler, or 2350 for the Emerson. The water should entirely immerse the bomb and avoid spattering by the stirrer. Then standardize with the new quantity of water. The conditions of combustion should be as closely as possible like those prevailing during regular coal analysis.

## DETERMINATION OF FUSIBILITY OF COAL ASH

This determination has become of increasing importance in recent years, especially in relation to mechanical stokers and gas manufacture. The composition of the ash, not its amount, is the deter-

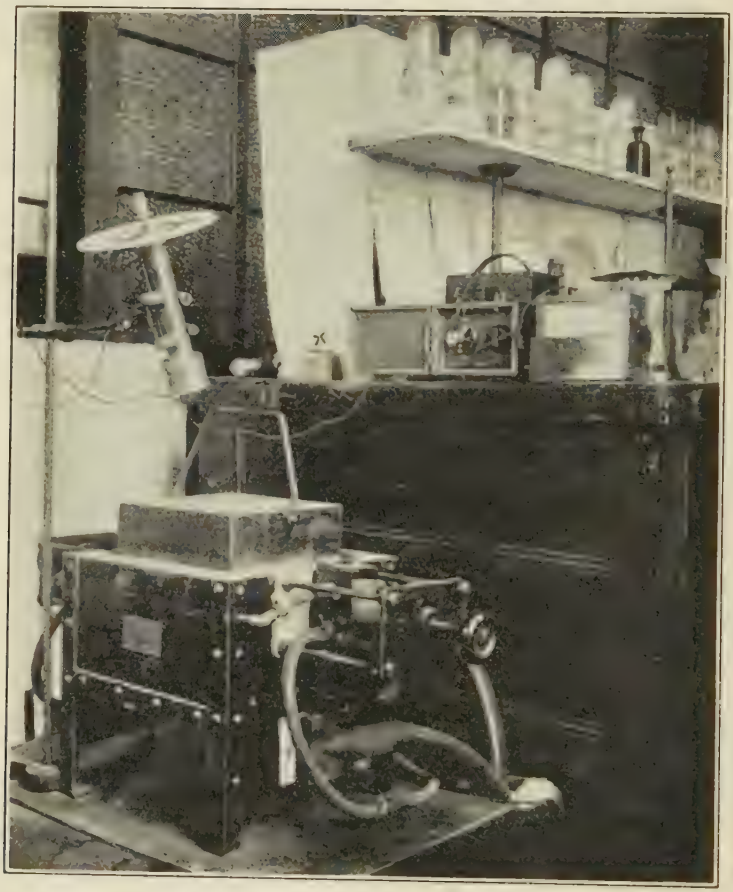


FIG. 135. Hoskins Electric Furnace, Optical Pyrometer in position, Also (X) Method of Supporting Cone in Graphite Block.

mining factor. Alumina is the most refractory constituent and its fusing-point, 2000 C., is lowered proportionately to the amounts of silica, alkalies, and iron present. In many coals the amounts of all but the latter do not lower the fusing-point sufficiently to cause

trouble, that is, below 1400° C. The amount of iron becomes then of supreme importance as the last straw that breaks the camel's back. This is popularly shown in the classification of coals as red ash and white ash. The condition of the iron is of great importance also, as in the ferric condition it has but slight effect, but in ferrous condition it lowers the fusion-point greatly. The influence of sulphur upon fusing-point probably depends upon the accompanying presence of iron as pyrites. In the coal bed in the presence of burning carbon the ferric oxide may be reduced to ferrous oxide or not, according to the care of the fire and the amount of oxygen supplied. This explains discrepancies occurring between the facts of clinkering of the coal on the grates and the fusing-point as determined in a laboratory furnace. The fusing-point varies in different types of furnaces for the same reasons. It seems safest to choose such furnaces in laboratory tests as give reducing atmospheres and hence lower fusing-point, indicating the possible danger.

A convenient furnace, for high temperatures especially, is the Hoskins Electric Furnace. The heat is generated by passing a heavy alternating current of low voltage through a series of carbon plates. Temperature is regulated by compression of these plates. This furnace uses a 60 cycle alternating current, 220 volts, about 40 amperes. The current is transformed by an air-cooled transformer to a current of 10 volts. The maximum temperature produced by the furnace is about 2000° C.

The coal is burned to ash at as low a temperature as possible in clay dishes. The ash is moistened with water and moulded into the shape of a Seger cone ($\frac{1}{2}$ in. by $2\frac{1}{2}$ ins.) by pressing into a mould conveniently made of lead. A piece of thin paper, moistened, is laid in the mould to facilitate removal of the cone. Some coals may require 10% dextrin paste as a binder, but it is usually unnecessary. The use of smaller cones has recently been advocated. The cones may be set in triangular holes in a Dixon graphite block and placed in the furnace so that the cone is horizontal. This position gives as concordant results as the vertical position, if not closer. The fusing-point is taken when the cone droops into a vertical position. The temperature must not rise too rapidly when near the fusing-point, about 5° C. per minute. The temperature is conveniently read by a fixed-focus total-radiation pyrometer or an optical pyrometer of the Wanner type. Reducing atmospheres preclude the use of metallic couples at high temperatures.

Note. — The methods in this chapter are based upon those in use at the Mt. Prospect Laboratory, of the Department of Water Supply, Gas and Electricity, New York City. The method for fusibility was obtained originally from the Laboratory of the Consolidated Gas Company, New York City.

### Conversion of Percentages of Constituents in a Substance from one Moisture Basis to Another, or from Dry to Wet Basis or Vice Versa [1]

The moisture content of a sample may vary in the original from that of the material analysed. For example in the analysis of coal the finely ground sample contains less moisture than the original lumps so that it is necessary to recalculate results to get the actual quantities present in the material as received. The results obtained bear the same ratio to the actual content as the total solids in the sample analysed bear to the total solids in the original sample. For example if the original lump contained 15% of moisture and the finely ground sample contained 10%, the ratio of total solids of the analysed to the original material would be 90:85 hence all results multiplied by 85/90 would give the true percentages existing in the original material.

**Rule.** — Multiply all percentages by the factor obtained by dividing the percent total solids in the material to which the conversion is desired by the total solids in the material analyzed.

**Examples.** — *A.* The moisture in the original sample was found to be 15%, the moisture in the powdered sample analysed was 10%, the ash in the latter was found to be 5%, what was the ash in the original sample? The total solids are 85 and 90 respectively. $85 \div 90 = .947$ and $5 \times .947 = 4.75\%$ ash in the original sample.

*B.* In case the examination was made of a dry material which originally contained 15% moisture the factor would be $85 \div 100 = .85$ so that 5% ash in the dry sample would be $5 \times .85 = 4.25\%$ in the original.

*C.* Should it be desired to figure from the wet basis to the dry basis, in case the sample analysed contained 15% of moisture and the ash was 5%, then on the dry basis this would be $(100 \div 85)5 = 5.88\%$.

This chapter was contributed by F. E. Hale, Director of Laboratories, Dept. Water Supply, Gas & Electricity, New York City.

### Short Method for the Ultimate Analysis of Coal [2]

For purposes of the engineer in boiler testing, the following method for determining the carbon, hydrogen, and oxygen in coals has been in practical use for a number of years with very satisfactory results.

An ordinary combustion of the coal is made with sodium peroxide by use of the calorimetric bomb or similar devices, especially adapted to total carbon or sulfur determination, as shown in Figs. 135a or 135b. The carbonate formed is discharged in any apparatus suitable for accurately measuring the carbon dioxide as shown in Fig. 135c.

[1] Method by W. W. Scott.

[2] By S. W. Parr, University of Illinois, Urbana, Illinois. Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

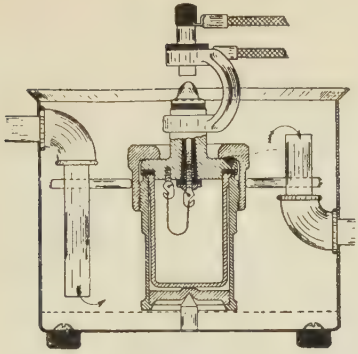


FIG. 135a

FIG. 135b

Courtesy of *Industrial & Engineering Chemistry.*

Having now the values in hand for sulfur and B. t. u., the calculations are of a simple order.

ULTIMATE ANALYSIS OF COAL, MOISTURE FREE

1. Weight of sulfur × 2777 = Calories from sulfur as $FeS_2$.
2. Weight of carbon × 8080 = Calories from carbon.
3. Total determined calories − (1 + 2) = Calories from available hydrogen.
4. $\frac{\text{Calories from available hydrogen}}{34{,}450}$ = Weight of available hydrogen.
5. Nitrogen present may be assumed as a constant of 1.25 per cent.
6. Then, by difference, 100 − (S + C + H + N + ash as weighed) = (O + H).[1]
7. 8/9 (O + H ) = Total oxygen.
8. 1/9 (O + H) = Combined hydrogen.
9. Then, combined hydrogen + available hydrogen (8 + 4) = Total hydrogen.

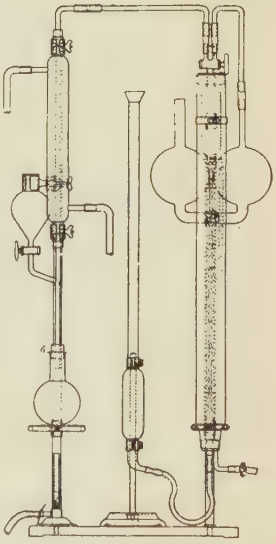


FIG. 135c

Courtesy of *Industrial & Engineering Chemistry.*

By deriving the factors as thus indicated, we have all of the constituents as obtained by ultimate analysis and with a degree of accuracy entirely commensurate with that secured by the longer process.

[1] The expression (O + H) refers to the total oxygen plus that amount of hydrogen necessary to combine with it to form water. This hydrogen is referred to as "combined hydrogen" to differentiate it from the "available hydrogen."

## WATER ANALYSIS

In actual practice the lack of real knowledge of methods for the determination of various impurities in the average water is rather astonishing. The impression is given the student that water analysis is difficult. The truth of the matter is that analysis of water depends upon certain definite and well developed methods, the only

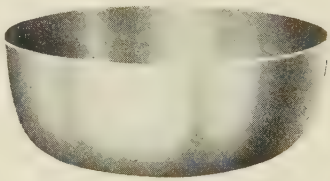


Fig. 135d. Platinum Evaporating Dish for Water Analysis.

difference being in the fact that the analyst is dealing with exceedingly small quantities.

It is possible to get complete and rapid results upon waters of all kinds if the analyst takes seriously reliable methods.

It shall be our purpose in the methods which follow to give a system of analysis whereby a complete analysis can be made, and to follow this up with optional methods which, individually, are equally as good as those occurring in the system of analysis, and in some cases more satisfactory where the laboratory has the required equipment.

## MINERAL ANALYSIS

### Outline of Procedure

50 cc. (Certified pipette or burette) evaporated to dryness at 270° F. in weighed platinum dish. Increased weight of dish represents **total solid residue.** (Can be used for $SO_4$ when sample is small.) Ignite for organic loss.

250 cc. Titrate with N/10 acid or alkali for **alkalinity or acidity.** (Can be re-used to make up volume of 500-cc. portion when water sample is small.) Methyl orange indicator.

100 cc. Titrate with N/10 $AgNO_3$ for **chlorine.**

100 cc. Acidify, boil, precipitate with $BaCl_2$, filter and weigh for **total sulphate.** (Use filtrate for Na and K when necessary.)

100 cc. Add 2 cc. of 10% $Na_2CO_3$, evaporate to dryness, add phenolsulphonic acid, dilute, then add excess of $NH_4OH$ for **total nitrate.**

500 cc. Evaporate to dryness (with a few cc. of concentrated HCl when very accurate $SiO_2$ figure is necessary) in No. 8 R. B. dish. Bake 30 minutes, cool, add boiling HCl (concentrated), dilute and filter.

| | | | |
|---|---|---|---|
| Precipitate is $SiO_2$ and silicate impurities (also $BaSO_4$). Unless great accuracy is necessary, it should be weighed as such, otherwise $SiO_2$ can be removed by HF and correction made. | Filtrate. Add a few drops of $HNO_3$, concentrate to 50 cc., cool, add $NH_4OH$, boil and filter. | | |
| | Precipitate (Fe, Al, Phos.) may be reported as such or as Fe and Al, after Qual. test for phosphate has shown same to be absent. Otherwise both Fe and Phos. should be determined and weight corrected. | Filtrate. Boil and add saturated Am. Oxalate drop by drop, boil and filter. | |
| | | Prec. Ca as oxalate, dry, ignite and weigh as $CaCO_3$ or CaO. | Filtrate Mg (and Mn), add 50 cc. of concentrated Sod. Phos. Solution, then 50 cc. of $NH_4OH$, stir well 2 minutes or more, let stand 4 hours, or more, filter and wash with 3% $NH_4OH$. Ignite and weigh. (Determine Mn separately and correct when necessary.) |

NOTE. — For industrial purposes the original addition of HCl is not always necessary and correction for $BaSO_4$, Phos., Mn and separation of Fe and Al can be dispensed with unless there is cause to suspect one to be present in material amounts.

In the matter of mineral analysis of water, it is not so hard to obtain a complete analysis of the water, including the non-incrusting or "nearly always" soluble materials as well as the incrusting materials, as it is to make numberless individual or independent tests, in the hope of drawing conclusions from same. The scheme of analysis which follows is used exclusively in the writer's labora-

tories, and when carried out as given, makes it possible to complete analysis of a water, or a group of waters numbering up to ten, in the period of eight hours elapsed time, or twenty-four hours, assuming the work is arranged in such a way that the magnesia precipitates are allowed to stand overnight before filtration. On another page will be found a skeleton form for this complete analysis, and this skeleton will serve as a rough guide to the more extended discussion which will follow.

The complete analysis considers the quantitative determinations of silica, iron and aluminum, calcium, magnesium, sodium and potassium, as bases, and carbonate, hydrate, nitrate, sulphate, chloride, and phosphate, as radicals or acids.

Prior to the starting of the analysis, the physical characteristics of the water should be noted, turbid waters should be filtered, the suspended matter analyzed separately when necessary, and the amount determined either by filtration and weighing of the separated material (alundum cones are very satisfactory), or by the difference between two residues, one of which represents the original water and one the filtered water. The mineral analysis should represent the filtered supply. This is due to the difficulty of getting uniform samples with suspended matter at different times.

### Silica, Iron, Aluminum, Calcium, Magnesium

Note. — If from qualitative observations the water contains considerable mineral matter, smaller quantities varying from 100 to 250 cc. may be taken, or if the sample is apparently distilled or condensed and contains very little mineral matter, 1000 cc. should be taken, the object being to obtain a residue neither too large nor too small. 0.4 to 0.6 gram is a good quantity to work on.

#### Silica

Evaporate over a free flame, then on $\frac{1}{4}$ in. asbestos board, to dryness, 500 cc. of original water, using a No. 8 porcelain dish. Bake at 110–130° C. or on an asbestos plate over flame for one-half hour. Moisten with 10 cc. of concentrated HCl, add 50 cc. of water, boil fifteen to thirty seconds and filter. Wash with hot water.

Note. — For great accuracy, evaporate twice to dryness as above, with the addition, prior to the sample going to dryness, of 10 cc. of HCl, allow to bake as above, following from there on the usual procedure for filtration.

The precipitate retained on the filter paper represents the silica or siliceous matter, including possibly barium sulphate. Ignite and weigh.

### Iron and Aluminum (Gravimetric)

The filtrate contains iron, aluminum, calcium, magnesium, possibly manganese, and phosphate. Bring to a boil, add two or three drops of conc. nitric acid and concentrate to about 25 cc. Remove from the hot plate or flame, add ammonium hydroxide in slight excess, boil for one or two minutes, and filter.

The precipitate contains iron, aluminum, and possibly phosphates. Burn and weigh as oxides of iron and aluminum, plus phosphates, and test 50 cc. of the original water with treatment in the usual way to determine whether or not phosphates are present. Where this precipitate of iron and aluminum oxides is greater than 0.01 gm. per liter or 8 parts per million, or where the separation of the iron and aluminum is advisable, the precipitate should be fused with eight or ten times its weight of potassium bisulphate, redissolved in water, the iron reduced to the ferrous condition with zinc, and titrated with potassium permanganate, recording the difference in weight between the original precipitate and the iron determination as aluminum oxide.

$$Fe \times 1.43 = Fe_2O_3.$$

### Calcium

The filtrate from iron, aluminum and phosphate precipitate contains calcium, magnesium, and possibly manganese. Concentrate to about 100 cc. Add to the hot ammoniacal solution a concentrated (saturated) solution of ammonium oxalate drop by drop, or add in small portions, crystals of ammonium oxalate. Allow to boil two minutes, stirring if necessary (on account of heavy precipitate and tendency to bump), remove, filter and wash. (Five complete washings are usually sufficient.)

Note. — Where great accuracy is desired, the precipitate on the filter should be redissolved in a small amount of hot, dilute, hydrochloric acid and reprecipitated with ammonium oxalate.

The calcium oxalate upon the filter paper can now be burned and weighed either as calcium oxide or calcium carbonate.

Note.— The burning of calcium oxalate to carbonate is not so difficult as it seems, as an intense heat is necessary to convert it to the oxide, and if the crucible is well watched and the flame gives just sufficient heat to carbonize and destroy the filter paper, there will be no chance whatever of any calcium oxide being formed, or any calcium oxalate being left. Where hypothetical combinations are used it is very convenient to have the calcium as carbonate without calculation. Where burned to the complete oxide it is frequently necessary to use a blast lamp, as large precipitates require a high temperature to reduce completely to oxide form.

### Optional (Volumetric)

Or it may be dissolved in 2% sulphuric acid and titrated with the standard solution of potassium permanganate. (N/50 $KMnO_4$ may be used.)

NOTE. — Where the volumetric method is to be used, five complete washings are not, as a rule, sufficient, as the presence of traces of ammonia salts, while not interfering in any way with the gravimetric determination, are prone to have considerable influence upon the volumetric results, due to the possibility of traces of ammonium oxalate still being present.

Fe Value $\times$ 0.895 = $CaCO_3$.
Fe Value $\times$ 0.5016 = CaO.
Fe Value $\times$ 0.3584 = Ca.

### Magnesium

*The filtrate contains magnesium.* Acidify with HCl, concentrate, if necessary, to 150 cc., add 25 cc. of saturated solution of ammonium sodium hydrogen phosphate ($NH_4NaHPO_4$. $4H_2O$, microcosmic salt), cool and make alkaline with ammonium hydrate. Allow to stand at least four hours, filter and wash with 3% solution of ammonium hydrate. Burn and weigh as $Mg_2P_2O_7$.

NOTE. — Accurate results are also obtained with the use of sodium phosphate added direct to the filtrate from the calcium precipitate without previously acidifying with acid, with 25 cc. to 50 cc. of ammonium hydrate added to make strongly alkaline, after which the solution should be very thoroughly stirred (for at least two minutes), using a rubber-ended glass rod. Allow to stand at least four hours.

For very rapid work in either case, if the magnesium solution after precipitation is cooled in ice-water, filtration can be frequently made in two hours' time.

For extremely accurate work the precipitate produced in either of the methods above should be redissolved in a little dilute HCl and the precipitations repeated.

### Sulphate

100 cc. of the water is slightly acidified with conc. HCl and 5 cc. of 10% $NH_4Cl$ solution added, brought to a boil, and if turbid is filtered and washed four or five times with boiling water. The clear or original water is now brought to a boil and 10% barium chloride added drop by drop to the boiling solution in slight excess. Boil ten minutes, stirring from time to time, if the precipitate is heavy. Remove and *allow to cool* prior to filtering. The precipitate consists of barium sulphate. Wash free from chlorides, testing with $AgNO_3$. Dry, ignite and weigh.

$BaSO_4 \times .411 = SO_4$.
$BaSO_4 \times .583 = CaSO_4$.
Milligrams of $BaSO_4 \times .338 = CaSO_4$ grains per gallon.

### Sodium and Potassium

The filtrate contains sodium and potassium and may be used for such unless the water is highly mineralized, in which case *a new portion, 100 cc. to 500 cc., should be taken.*

Evaporate to dryness, add saturated solution of barium hydrate in excess, filter, wash with hot water, add to the filtrate ammonium carbonate in excess and a few drops of ammonium oxalate, boil, filter, evaporate again to dryness and dry at a high temperature to expel excess of ammonia salts. Redissolve, add slight excess of ammonium carbonate again and continue until no further precipitate is formed on such addition. Evaporate to dryness in a weighed platinum dish, remove ammonium salts by high-temperature drying, and weigh the combined chlorides of sodium and potassium. Moisten with about 25 cc. of water and a few drops of HCl and add from 1 cc. to 5 cc. of 10% solution of platinic chloride (1 cc. to each 25 milligrams to 30 milligrams of total chlorides). Evaporate to dryness on the water bath, take up and wash with 95% alcohol until filtrate is free from color. Dry, redissolve precipitate, washing through the filter paper in hot water. Evaporate again to dryness and weigh as $K_2PtCl_6$.

$$K_2PtCl_6 \times .161 = K.$$
$$K_2PtCl_6 \times .307 = KCl.$$

Deduct from combined weight of chlorides. Remaining $NaCl \times .394 = Na$.

Note. — When separation is not necessary, the combined chlorides are calculated as sodium chloride and reported as sodium and potassium chlorides.

### Alkalinity

In ordinary cases titrate with N/10 or N/50 $H_2SO_4$, using methyl orange as indicator. Special cases will be considered later.

**Reagents.** — Sulphuric acid, N/10. Methyl orange. Phenolphthalein.

**Operation.** — 250 cc. of water in a 400 cc. beaker or a casserole are titrated with N/10 $H_2SO_4$, using two to five drops of methyl orange indicator (or 50 cc. can be similarly titrated with N/50 $H_2SO_4$).

Calculate for 250 cc. sample.

No. cc. $\times$ 4 $\times$ .005 = gms. per liter $CaCO_3$.
No. cc. $\times$ 4 $\times$ 58.4 $\times$ .005 = grs. per gallon $CaCO_3$.
Or cc. $\times$ 1.168 = grs. per gallon $CaCO_3$.

Distilled water, and neutral waters containing magnesium chloride and magnesium sulphate frequently give an alkaline reaction when used with methyl orange. In such cases from .2 to .8 cc. of N/10 acid are required to discharge the alkaline color of the methyl orange. Such a procedure would suggest to the operator that the waters were alka-

line. However, if such neutral waters are boiled with phenolphthalein as an indicator for twenty minutes and no pink color develops, the waters are not alkaline but neutral. The use of a blank of .2 cc. is of no value under such conditions and it appears to the writer as much the safest way when the titration is under 1 cc. of N/10 acid that the water be boiled with phenolphthalein in an effort to determine absolutely whether this water is alkaline, due to the presence of a carbonate as indicated by the methyl orange, or whether the alkalinity is entirely due to the hydrolizing of the calcium or magnesium base present in the absence of alkali. When no pink color is produced the water should be pronounced neutral.

Phenolphthalein may also be used as indicator on another 250 cc. portion, using the above procedure. This titration in connection with the methyl orange titration makes possible a determination of the relation of carbonate, bicarbonate and caustic alkalinity.

### Acidity

For acidity use N/10 $Na_2CO_3$ and 250 cc. of water.

| Acidity due to | Indicator. | Hot or Cold. |
|---|---|---|
| Carbonic and sulphuric acids, also Fe and Al sulphates | Phenolphthalein | Cold |
| Sulphuric acid, also Fe and Al sulphates | Phenolphthalein | Boiling |
| Sulphuric acid alone. When desired, 20 cc. of N/10 $H_2SO_4$ may be added. Boil fifteen to twenty minutes, cool and titrate, noting the excess of acidity over the original 20 cc. | Methyl orange | Cold |

### Free Carbonic Acid

**Reagents.** — Either standard N/10 sodium carbonate or standard N/22 sodium carbonate. For the latter dissolve 2.41 grams of dry sodium carbonate in one liter of distilled water which has been boiled and cooled in a carbon dioxide free atmosphere. Hold both solutions in glass bottles protected by tubes filled with soda-lime.

One cc. of N/10 $Na_2CO_3$ = 2.2 milligrams of $CO_2$.
One cc. of N/22 $Na_2CO_3$ = 1.0 milligram of $CO_2$.

**Operation.** — With N/10 sodium carbonate titrate 250 cc. of the sample in a 400 cc. beaker, using phenolphthalein as indicator. First faint but permanent pink denotes end-point.

Using 250 cc.

No. cc. of N/10 $Na_2CO_3 \times 8.8$ = $CO_2$ parts per million.
No. cc. of N/10 $Na_2CO_3 \times .513$ = $CO_2$ grains per gallon.

With N/22 sodium carbonate solution, use 100 cc. of the sample, preferably in 100 cc. Nessler tube, titrate and rotate the tube until a faint but permanent pink color, persisting for 30 seconds without fading, is produced, using phenolphthalein as indicator.

Using 100 cc.

No. cc. of N/22 $Na_2CO_3 \times 10 = CO_2$ parts per million.
No. cc. of N/22 $Na_2CO_3 \times .583 = CO_2$ grains per gallon.

### Chlorine

Titrate 100 cc. of the water, using 1 cc. of 10% potassium chromate as an indicator, with N/10 $AgNO_3$ to first permanent indication of the red silver chromate. (Acid waters should be neutralized and sulphide waters boiled with a drop or so of nitric acid and then neutralized for reliable results.)

No. cc. $\times$ 3.42 = grs. per gallon of NaCl.
No. cc. $\times$ 58.46 = parts per million of NaCl.
No. cc. $\times$ 35.46 = parts per million of Cl.

Note. — Where qualitative test shows chlorine to be high, smaller portions of the sample should be taken, either by certified pipette, or burette, and when the titration with N/10 $AgNO_3$ is less than .2 cc., N/50 or N/100 $AgNO_3$ should be used for accuracy.

### Ammonia and Its Compounds

Place 500 cc. or less in an 800 cc. Kjeldahl flask, make alkaline and distill into N/10, or weaker, HCl, titrate back using cochineal indicator or Nesslerize, by distilling off three 50 cc. portions of a 500 cc. sample, to which has been added a slight excess of pure sodium carbonate, catching the portions in Nessler jars. The apparatus should be cleaned out, previously, by a similar procedure with pure water. To each 50 cc. portion 2 cc. of Nessler's solution are added and comparison made with standards containing known amounts of ammonia.

**Nitrates.** — A volume of 500 cc. of the water is made slightly acid and boiled, then made alkaline with sodium hydroxide, 10 grams of powdered aluminum added and 150 cc. distilled off into a boric acid solution (5 g. per 100 cc.) methyl orange indicator is added and the ammonia titrated with standard acid. Correct to equivalent $HNO_3$.

### Hydrogen Sulphide

Due to the fact that hydrogen sulphide is frequently very transient and often oxidizes to sulphate in transit, it is advisable to collect this sample in a special container at the point of sampling. Two or three bottles holding exactly 250 cc. of water each, are used, each bottle containing 50 cc. of N/100 iodine solution. After filling, the bottle is sealed. The sample is titrated with standard N/100 sodium

thiosulphate upon receipt at laboratory, at which time a blank is run, using 50 cc. of iodine solution made to mark with distilled water. The difference between the titration of the sample and the blank represents hydrogen sulphide present.

Iodine value $\times$ 0.1263 $\times$ 4 = sulphur value grams per liter.

For samples received in the laboratory, where the sulphide odor is marked, or where the sample is slightly turbid, and the odor is gone, and a method is desired, or an estimated figure asked for, proceed as follows:—

100 cc. of the water taken under the same conditions as the sample for Total Sulphate is oxidized with bromine, and, after a sufficient period of boiling, the sulphates are precipitated, using barium chloride in exactly the same manner as recommended for the sulphate determination.

The difference between this total sulphur and fixed sulphur, — as the regular sulphate determination is called, represents sulphur existing either as hydrogen sulphide or as separated sulphur, originally hydrogen sulphide, and should be calculated as such.

### Oil

Frequently waters from condensing engine, or after passing heaters or oil separators, still contain oil in small quantities. The following method has been found most satisfactory.

**Reagents.** — *Ferric Chloride Solution.* (10 grams of iron dissolved in 200 cc. of HCl, oxidized with $HNO_3$ and made to one liter.)

*Ammonia* C.P.

Note. — If the oil exceeds 0.4 grain per gallon, use 500 cc. or less for the determination; if below 0.4 grain per gallon use 1 liter.

**Operation.** — Add to the water taken in a large beaker or flask 5 cc. of the "ferric chloride" solution and heat nearly to boiling; then add ammonia in excess, to precipitate the iron (which precipitate contains all the oil), and boil for two minutes.

Allow to stand a few minutes and filter through a 15 cm. filter paper which has been previously extracted with ether, transferring the precipitate on to the paper with hot water, and washing three or four times with hot water. Then dry both filter and precipitate in the water oven at 100° C. and when dry, extract with ether in the Soxhlet in the usual way, evaporate the ether extract and weigh the remaining oil.

## Dissolved Oxygen

### Winkler Method

**Reagents.** —*Manganous Sulphate Solution.* 48 grams of manganous sulphate dissolved in 100 cc. of distilled water.

*Iodide Solution.* 360 grams of NaOH and 100 grams of KI dissolved in 1 liter of distilled water.

*Concentrated hydrochloric acid, or sulphuric acid sp.gr.* 1.4 (*dilute* 1 : 1).

*Sodium Thiosulphate Solution.*[1] N/100 solution is made as needed from the N/10 stock solution.

*Starch Solution.* — The starch should first be made into a thin paste with cold water and about 200 times its weight of boiling water stirred in and boiled for a few minutes. A few drops of chloroform will assist in preserving this solution.

**Collection of Sample.** — A small-necked, 250 cc. bottle should be used, etched or otherwise marked, with its exact volume previously determined. The collection should be so arranged as to exclude outside air and result in several continuous changes of the contents before stoppering, care being taken to exclude air bubbles.

**Operation.** — To sample as received add, in both cases by pipette, delivering below surface of water and away from the air, 2 cc. of manganese sulphate reagent and 2 cc. of NaOH,KI solution. Restopper and shake thoroughly. After precipitate has settled add 2 cc. of HCl or $H_2SO_4$ and again mix by thorough shaking until precipitate has completely dissolved, transfer 100 cc. to flask, and titrate with standard sodium thiosulphate, using starch as indicator near end as the color approaches a faint yellow.

N = cc. N/100 thiosulphate solution.
V = capacity of bottle less 4 cc. (vol. $MnSO_4$ and KI solutions).
O = the amount of oxygen in parts per million in water saturated at the same temperature and pressure.

(1) Oxygen in p.p.m. $= \dfrac{.0008N \times 1{,}000{,}000}{100} = .8N.$

(2) Oxygen in cc. per liter = .7 oxygen p.p.m.

(3) Oxygen per cent saturation $= \dfrac{\text{Oxygen p.p.m. (observed temp. and pres.)}}{\text{Saturation oxygen p.p.m. (observed temp. and pres.)}}$

[1] Not permanent; should be frequently restandardized against N/100 potassium bichromate.

The addition of 5 cc. of chloroform plus 1.5 grams of sodium or ammonium carbonate to each liter of solution on mixing will improve its keeping quality.

N/40 sodium thiosulphate containing 6.2 grams of C.P. recrystallized salt per liter may be preferred to N/100 strength. 1 cc. of this solution is equivalent to 0.2 milligram of oxygen by weight or 0.1395 cc. of oxygen by volume, standard conditions.

## HARDNESS

### Total Hardness

The most accurate method for total hardness is by calculation of the calcium and magnesium determined gravimetrically as previously outlined, calculating the calcium as calcium carbonate and the magnesium to its calcium carbonate equivalent in terms of parts per million. However, where only the hardness is desired, gravimetric methods are cumbersome and the following are accepted as standard.

The standard method for the determination of total hardness, as well as temporary and permanent, depends upon the action of the lime and magnesium in solution upon soap, the soap added in a very dilute solution in alcohol. Total hardness represents the total soap acted upon by the water in its original state, permanent hardness represents the total soap acted upon by the water after the water in question has been thoroughly boiled and separated from the suspended matter, and temporary hardness represents the difference between the total hardness and the permanent hardness, and while it is supposed to represent combined carbonates of lime and magnesium, and the permanent hardness is supposed to represent lime and magnesium in other forms than carbonate, this is rarely so due to the fact that a certain material amount of carbonate of lime and magnesium is soluble in water, even in the absence of carbon dioxide gas. The reagents used are *standard soap solution* and *standard calcium chloride solution,* the latter being made under such conditions that 1 cc. of the solution is equivalent to 0.2 milligram of calcium carbonate.

### Preparation of Solutions

0.2 gram of pure calcium carbonate is dissolved in a small amount of dilute HCl, taking pains to avoid any loss due to effervescence or spattering. Evaporate the solution to dryness several times to remove excess acid. Dissolve in distilled water and make up to 1 liter.

*Standard soap solution* is obtained by dissolving approximately 100 grams of dry castile soap in 1 liter of 80% alcohol. This solution should stand several days. For standardizing, this solution should be diluted with alcohol (70% to 80%), until 6.4 cc. when added to 20 cc. of standard calcium solution will produce a permanent lather. Usually less than 100 cc. of the original soap solution will make 1 liter of standard solution.

For standardizing, use a 250 cc. glass-stoppered bottle, add 20 cc. of calcium solution with 30 cc. of distilled water. The soap solution should be added from a burette, approximately .2 cc. at a time, after which the bottle is shaken vigorously until the lather formed remains un-

broken for five minutes after shaking and after the bottle has been placed upon its side.

NOTE. — Pure potassium oleate and potassium carbonate may be used in place of soap.

**Operation.** — Fifty cc. of the water in question are measured into a 250 cc. bottle, the soap solution added, approximately .2 cc. at a time, and in the same manner as described for the standardizing of said soap solution.

In making this determination there is frequently noted a false end-point sometimes known as the magnesium end-point. To avoid error, it is advisable, after completing the titration, to read the burette, add 0.5 cc. more of the soap solution and shake well. If magnesium has been responsible for the false end-point, after such addition the lather will again disappear, and titration should be continued until a new and true end-point is reached. It is advisable to determine the strength of the soap solution from time to time, as it is very prone to change upon standing. Results should be recorded in terms of calcium carbonate, parts per million. There are various other means of reporting. The English degree, frequently noted as Clark degree, represents grains of calcium carbonate per Imperial gallon and should be multiplied by 14.3 to give parts per million. Conversely, the result obtained in parts per million divided by 14.3 will give Clark, or English degrees. French degrees represent parts per 100,000 of calcium carbonate and should be multiplied by 10 to give parts per million. Conversely, division of the result obtained above by 10 will give French degrees. German degrees represent parts per 100,000 of calcium oxide and should be multiplied by 17.8 to give parts per million of calcium carbonate. The determination of hardness is not reliable on account of the varying action of calcium and magnesium salts, and should never be resorted to when possible to determine these bases direct.

For *permanent hardness* the standard soap solution is used as above stated. The water, however, is boiled gently for one-half hour, allowed to cool, made to volume with boiled and cooled distilled water and filtered, after which the above method is used. The difference between total hardness and permanent hardness is supposed to represent temporary hardness. The *alkalinity* determination given on a previous page is a much more accurate method of determining temporary hardness, however, and is also much more easily carried out. When total hardness and alkalinity are determined, permanent hardness would be the difference between these two figures. For comparative use as against *total* and *permanent* hardness determined as such, the results would be much different, as the alkalinity determination of all the carbonates would give a permanent hardness representing absolutely non-carbonate hardness; whereas the determined permanent hardness would contain a material amount of com-

bined carbonates of lime and magnesium. The American Public Health Association, Committee on Standard Methods of Water Analysis, recommend that the determination of permanent hardness by the soap solution be discontinued in connection with softening process, as it is so unsatisfactory in general practice.

**Total Mineral Content.** — Evaporate 50 cc. to dryness and bake for 30 minutes at 130° C. Weigh as total solids.

Weight × 1168 = grains per gallon.
0.1 milligram = 2 parts per million.

If much organic matter is present, after weighing, ignite at red heat to destroy organic matter, add a little ammonium carbonate, heat to 130° C. and again weigh, repeat until constant.

## METHODS OF REPORTING AND INTERPRETATION

The manner of reporting the results of a mineral analysis of any water calls for as much thought and uniformity as the methods of analysis themselves, and in this department there is much less uniformity than in the case of analytical methods. Undoubtedly, the ideal method of reporting is that which gives results in Ionic form (positive and negative radicals), in terms of parts per million or grains per gallon. The latter term is purely American and would have to be converted for comparison with results obtained in almost any foreign country. Parts per million, though newer and still unfamiliar to all but professional and scientific men, is gaining gradually a strong foothold, and the consideration of this terminology with the Ionic form of reporting will be considered prior to the discussion of hypothetical combination and grains per gallon.

Mr. Herman Stabler,[1] and R. B. Dole,[2] of the United States Geological Survey, have devised and simplified certain calculations and formulas, which greatly assist in the interpretation, comparison, and classification of waters for Industrial and Irrigation[3] purposes. Formulas with reference to dissolved solids will be the only ones discussed here. The following table gives reaction coefficients:

| Positive Radicals | Reaction Coefficients | Negative Radicals | Reaction Coefficients |
|---|---|---|---|
| Ferrous Iron (Fe) | 0.0358 | Carbonate ($CO_3$) | 0.0333 |
| Aluminum (Al) | .1107 | Bicarbonate ($HCO_3$) | .0164 |
| Calcium (Ca) | .0499 | Sulphate ($SO_4$) | .0208 |
| Magnesium (Mg) | .0822 | Chlorine (Cl) | .0282 |
| Sodium (Na) | .0435 | Nitrate ($NO_3$) | .0161 |
| Potassium (K) | .0256 | | |
| Hydrogen (H) | .992 | | |

Using the above table, the parts per million of each radical multiplied by its reacting coefficient will give its reacting value, and in the formulas which follow this will be indicated by "r" prefixed to the chemical symbol of the radical.

For checking the accuracy of the analysis, the sum of the positive reacting values should equal the sum of the negative reacting values, and the formula,

$$100\,\frac{\text{r. Pos.} - \text{r Neg.}}{\text{r. Pos.} + \text{r Neg.}} = \text{E, the percentage error of the analysis.}$$

The value of this error should never exceed 5 for waters of 100 p.p.m. or more of dissolved solids, and should be 2 or less.

[1] Eng. News, 60, 355, 1909.

[2] Water Supply Paper No. 274, p. 165, Water Supply Paper No. 254, J. Ind. and Eng. Chem., 6 (1914), No. 7, p. 710.

[3] U. S. G. S. W. S. Paper, 274, p. 177.

In ordinary analysis, silica, iron and aluminum are present in such small quantities that they may, for simplicity's sake, be ignored. The following formulas are given without comment, as full details can be found in Water Supply Paper No. 274.

### Water Softening

**For 1000 Gals. of Water.** — Pounds of lime (90% CaO) required.

$$= 0.26(\mathrm{rFe} + \mathrm{rAl} + \mathrm{rMg} + \mathrm{rH} + \mathrm{rHCO_3} + .0454\ \mathrm{CO_2}).$$

Pounds of soda ash (95% $Na_2CO_3$) required

$$= 0.465(\mathrm{rFe} + \mathrm{rAl} + \mathrm{rCa} + \mathrm{rMg} + \mathrm{rH} - \mathrm{rCO_3} - \mathrm{rHCO_3}).$$

NOTE. Dr. Hale states the following. Instead of the extended formulæ of the Ionic system, I much prefer my simple formulæ.

(Alkalinity $\times$ .44 + free $CO_2$) $\times$ .0106 = lbs. of CaO per 1000 gals. of feed water.

Also (Total hardness – total lime) $\times$ .0047 = lbs. of CaO per 1000 gals. of feed water, or total magnesia as $CaCO_3$.

(Total hardness – alkalinity) $\times$ .009 = lbs. of $Na_2CO_3$ per 1000 gals. of feed water, expressed as $CaCO_3$.

### Foaming and Priming

Foaming coefficient F = 2.7 Na.

Taking into consideration the various boilers and the action of various waters in practice, the following approximate classification of waters for foaming conditions is of value:

Non-foaming, F = 60 or less.
Semi-foaming, F = 60–200.
Foaming, F = 200 or more.

### Corrosion

*For Acid Waters*

Coefficient of corrosion C

$$= 1.008(\mathrm{rH} + \mathrm{rAl} + \mathrm{rFe} + \mathrm{rMg} - \mathrm{rCO_3} - \mathrm{rH_2CO_3}).$$

*For Alkaline Waters*

$$\mathrm{C} = \mathrm{rMg} - \mathrm{rH_2CO_3}.$$

If C is positive, water will corrode.

If C + .0503 Ca is negative, water will not corrode on account of the mineral materials in the water.

If C is negative, but C – .0503 Ca is positive, the water may or may not corrode.

### Scale

$$SiO_2 + 2.95\ Ca + 1.66\ Mg = \text{scale p.p.m.},$$

or

$$^{1}\ (.00833\ Sm + .00833\ Cm + .3\ rFe + .142\ rAl) + .168\ rMg + .492\ rCa = \text{scale lbs. per 1000 gallons.}$$

There are also formulas given in the above-mentioned Bulletin on soap cost, lime, soda, soda ash, cost hard scale (pounds per 1000 gallons) and a hardness coefficient of the scale formation.

### Irrigating Waters

*Alkali Coefficient*

(*a*) When $Na - .65\ Cl$ is zero or negative.

$$\text{Alkali coefficient, } k = \frac{2040}{Cl}.$$

(*b*) When $Na - .65\ Cl$ is positive, but not greater than $.48\ SO_4$,

$$\text{Alkali coefficient, } k = \frac{6620}{Na + 2.6\ Cl}.$$

(*c*) When $Na - .65\ Cl - .48\ SO_4$ is positive,

$$\text{Alkali coefficient, } k = \frac{662}{Na - .32\ Cl - .43\ SO_4}.$$

Classification on basis of alkali coefficient:

| Alkali Coefficient | Class | Remarks |
|---|---|---|
| More than 18... | Good... | Have been used successfully for many years without special care to prevent alkali accumulation. |
| 18 to 6 ..... | Fair.... | Special care to prevent gradual alkali accumulation has generally been found necessary except on loose soils with free drainage. |
| 5.9 to 1.27 ..... | Poor ... | Care in selection of soils has been found to be imperative and artificial drainage has frequently been found necessary. |
| Less than 1.2... | Bad.... | Practically valueless for irrigation. |

[1] Can be omitted or ignored unless suspended matter, silica, etc., are present in large quantities.

### Hypothetical Combinations

The use of hypothetical combinations in the reporting of a mineral water is frequently of value, in that it gives a more rapid way of placing in simpler terms the principal materials present in the water. It should never be assumed from the hypothetical combinations that the materials so reported are present in the water in that particular form, but it is assumed by most, that the form in which such materials are reported will represent the condition in which those materials will combine when the water is subjected to increased pressure and increased temperature. In other words, the hypothetical combinations most generally in use represent the way materials will appear when combined, due to the law of mass action under steam-boiler conditions.

For such purpose the method which takes care of the insoluble materials or materials leaving the water first is the most common method in use. This method combines as follows: Where the sum of the sulphate and carbonate radicals exceeds that of lime and magnesia as bases, the magnesia is first calculated to carbonate, the remaining carbonate is combined with lime, the remaining lime with sulphate and the remaining sulphate with sodium. This also takes care of the general condition where the carbonates alone are in excess of the combined carbonates of lime and magnesium, in which case the remaining carbonate naturally would be calculated to sodium and all the sulphate, as well as chloride, also, calculated to sodium. Where, however, the sum of the bases is greater than the sum of the carbonate and the sulphate radicals, two possible conditions or combinations exist. Where magnesium chloride is present in the water, the sum of the acids calculated to the soda radical should be greater than the total mineral residue. Partially decomposed magnesium chloride is indicated in this way, also the fact that magnesium chloride has a lower molecular weight than sodium chloride, which condition would be indicated in such a comparison. When this case exists, the sulphate is first calculated to calcium, the remaining calcium to carbonate, the remaining carbonate to magnesium, the remaining magnesium to chloride, the remaining chloride to sodium. Where the total mineral residue is greater than the sum of the acids and where nitrates are present, we then have nitrate of lime, which is assumed the commoner form than nitrate of magnesium, and the calculations are as follows: All the sulphate is calculated to lime, all the magnesium to carbonate, the remaining carbonate to lime, the remaining lime to nitrate, the remaining nitrate to sodium, and all the chlorides to sodium. In acid waters naturally the lime and magnesia, as well as the iron and aluminum, are calculated to the acid present in the greatest excess. These methods of calculation will give certain materials frequently found in

scale formation and materials frequently supposed to cause certain characteristic troubles in either steam or domestic usage. It is possible in a purely qualitative way to judge or interpret the water on the basis of the lime and magnesium salts, for incrustation, and of the alkali salts for other troubles in boiler practice, also from the standpoint of irrigation, the various forms of the alkali salts as black and white alkali without the necessity to use the formulas already considered.[1]

[1] This chapter was contributed by D. K. French, Director of the Laboratory, Dearborn Chemical Co., Chicago, Ill.

## GAS ANALYSIS

### SAMPLING

The process[1] consists in the insertion of a suitable tube into the flue or duct, and the withdrawal of the gas sought, by some sort of pump.

**Tubes.** — The tube employed varies with the nature of the gas and its temperature. Ordinarily, a combustion tube a meter long of 16–17 mm. outside diameter, which has been drawn down to 7 mm. at one end, to facilitate the attachment of rubber tubing, is used. These soften at about 500° C. For higher temperatures, we have a choice of quartz, porcelain tubes of about the same dimensions, or water-cooled metal tubes. Uncooled metal tubes cannot be employed above 250° without danger of reduction of the oxides of the metals

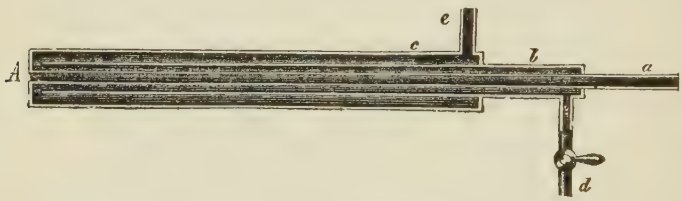



Fig. 136. Gas Sampling Tube.

composing the tube, by the carbonic oxide contained in the gases.[2] If porcelain tubes be used, they should be glazed within and without, to prevent the transfusion through them of the lighter gases like methane and hydrogen: they, as well as glass tubes, should be warmed before insertion into a hot flue. The construction of the water-cooled tubes will be evident from Fig. 136.

For cooling the gas, the tube should not be inserted to its full length. Rolls of wire gauze can be inserted near the cool, drawn-out end of the tube: these will serve for the removal of soot and dust. The removal of dust may be further effected by the use of plugs of asbestos or glass wool.

The place from which the gas is collected should be so chosen as to give a representative sample, and all openings, except those in-

[1] See also Bureau of Mines Bulletin, No. 97, "Sampling and Analyzing Flue Gases."

[2] Fischer, "Technologie der Brennstoffe," 1880, p. 221, cites an instance in which $CO_2$ was changed from 1.5 in the mixture, to 26% by the passage through an iron tube heated to dull redness.

tended for the inlet of air, stopped up. In a circular duct or chimney the average velocity of the gases is usually at a point one-third the distance from the wall to the center. In case of a boiler, the setting should be carefully inspected, all cracks filled with mortar, and the clean-out doors made tight. The fact that bricks themselves are porous must not be lost sight of, and new settings should be sized and given a coat of whitewash. If possible, the tube should be inserted below the damper to avoid leakage from that source. A second hole should be made for the introduction of an oil tube for the thermometer. The joints around these tubes should be made tight with mortar, plaster of Paris, or in the case of a temporary connection, putty or wet cotton waste. Care should be taken not to insert the tube so close to the source of heat as to withdraw the gases in a dissociated or partially decomposed condition. For sampling gases from different zones of a blast furnace, water-cooled tubes are made which can be screwed together to produce the desired length.

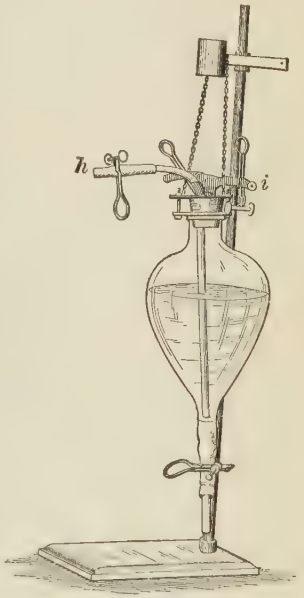


FIG. 137. Gas Container.

**Containers for Samples.** — These are of glass, preferably of the shape shown in Fig. 137. Being pear shaped, the vessel is completely emptied, leaving no liquid to exercise a solvent action on the gas. The tubing shown in the figure is of lead, which can be safely used for chimney gases after it becomes attacked by them. Its obvious advantage is found in the fact that it bends rather than breaks. Glass bottles — parts of the aspirator just described — may be used; the rubber connection should be thick, carefully wired on and provided with screw pinch-cocks. The long tube should carry a short piece of rubber tubing within the bottle reaching to its side; by tipping it the water can be more completely run out through this tube. The use of metal containers in general is not recommended, as those of zinc or galvanized iron are attacked by carbon dioxide; where the gases do not act upon the metals they may of course be advantageously employed. To ensure tightness, the rubber stoppers used should be held in by screws which fit into a brass plate on top of the stopper and into wire loops about the neck of the bottle. This compresses the stopper about the tubes and into the bottle neck, making a thoroughly tight joint. Or the brass plate may be replaced by a piece of sole leather and wire passed over this after the manner of wiring down the bottles containing carbonated waters.

The use of rubber bags is not to be recommended, as they absorb certain gases and are oxidized by others: the most satisfactory

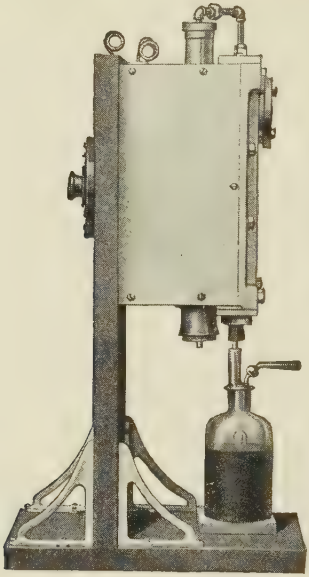


FIG. 137a. Laboratory Unit.
Courtesy of U. S. Ozone Co., Scottsdale, Pa.

containers are glass tubes provided with drawn-out ends which can be sealed in the lamp flame.

In connecting up the sampling tube, container and pump, the use of rubber tubing is to be avoided as much as possible for the reason just given.

## MEASUREMENT OF GAS IN LARGE QUANTITIES. METERS

Several types of instruments are available for this purpose.

The wet meter, The dry meter } Measure total gas passed — not for acid gases.

The Pitot tube, The orifice meter, The anemometer } All these measure velocity simply.

The **wet meter** consists of a cylindrical drum divided into four spiral compartments, suspended in a bath of water, surrounded by a tight casing: the pressure of the gas causes the drum to rotate, emptying a drumful of gas into the casing and pipes. It must be set level, the water level carefully adjusted to the mark on the glass gauge, with its top open, as well as the inlet and outlet pipes of the meter. The higher the water level the faster the meter. The **dry meter** consists of a pair of metal bellows, with sides of leather soaked in oil, on either side of a diaphragm, and connected with slide valves so that a bellowsful of gas is alternately emptied into the upper part of the meter and piping. The vibrations of the bellows produced by the gas pressure are transmitted to clockwork and indexes. It is to be noted that the indexes apparently read one-tenth of the actual volume passed: the index must make a complete circuit to register the amount stamped on the dial. A small index and dial are usually present for testing the meter, and a tolerance of 2% is allowed by law. This testing is done by meter-provers, carefully calibrated gas holders kept at constant temperature and the rate determined at different speeds. The meter-provers are, in their turn, calibrated by a cubic foot, standardized at the Bureau of Standards. It should be noted that all this calibration is corrected, not to standard conditions (0° C. and 760 mm.), but to the cubic foot as fixed by law — gas saturated with moisture at 60° F. and 30 inches.

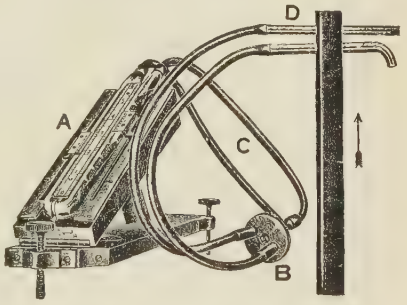



FIG. 138. The Pitot Tube.

**The Pitot Tube.** — Fig. 138. This consists of two glass tubes, *D*, of about $\frac{3}{16}$ inch internal diameter, inserted in the gas stream: one is bent at right angles and is set so that it receives the impact of the gas movement; the other merely registers the pressure of the gas in the pipe. The point of insertion of these tubes in the chim-

ney or duct should be in a long straight run of pipe, so as to be as free from eddies as possible. Davis [1] says that authorities differ as to whether the tubes should be a third or one-sixth of the diameter from the circumference to show the mean speed: he states further that each flue or chimney is a separate problem and as a result of hundreds of measurements there seems to be "no settled proportionate distance corresponding to the mean velocity."

The glass tubes are connected by rubber tubing, $C$, through a reverser, $B$, with a U-tube $A$, which is either set vertically, inclined 30°, or one in ten — this carries a vernier reading to hundredths of an inch so that readings to thousandths are feasible. The U-tube is filled with solutions of different specific gravity, although ether of 0.74 sp.gr. is the one commonly employed. The difference between the arms of the U-tube represents the difference between the kinetic and static pressures of the gas in the flue or chimney.

The formula for calculating the velocity recommended by W. W. Scott is

$$V = 1290 \sqrt{\frac{\frac{1}{2}h(1 + .002176t)}{BM}}$$

where $h$ = vertical differential of gauge reading in terms of inches of water. Half the reading is taken, as the actual reading is double that due to flow pressure alone. $B$ = barometric pressure of the gas in inches of mercury (29.92″). $M$ = specific gravity compared with $H = 1$. Air = 14.39. $t$ = temperature of the gas. $V$ = velocity in feet per second. The formula $V = 42\sqrt{h}$ gives fairly accurate results.

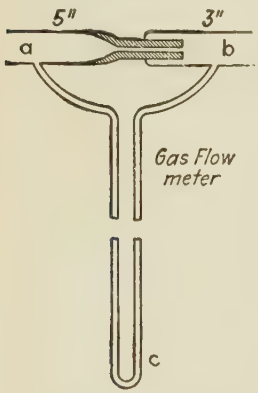



Fig. 139. Gas Flow Meter.

**The Orifice Meter.** — In this the same principle is used as in measuring water, by determining the diminution in pressure as registered on delicate gauges before and after the gas has passed through a standard orifice. It is largely used for measuring natural gas.

**The Anemometer** is used ordinarily for measuring currents of air leaving or entering a room, analogous to its employment in meteorology.

**The Gas Flow Meter.** — This consists of a tube $a$, into which capillaries $b$ of different sizes can be inserted by a rubber stopper (one at a time). On either side of the capillary is a T, the stems of which are joined together, making a U gauge $c$. This, when filled with water, shows the difference in pressure of the gas before and after passing through the capillaries. The apparatus is calibrated by a wet or dry meter. It has a capacity of from 0.5 to 500 liters per hour. See Fig. 139.

[1] "Handbook of Chemical Engineering," 1, 197, also for the tables for its use.

### Gas Burettes for Measuring Small Quantities of Gas

Here may be mentioned the Hempel gas burette, made for accurate work with a compensation tube; the bulbed Orsat or Bunte burette; the separatory funnel and graduate.

**The Hempel Gas Burette,** Fig. 140, consists of a 100 cc. burette graduated in fifths of a cubic centimeter, provided with a short capillary at the top and closed with a rubber connector and pinchcock and a wider tube at the bottom, over which the $\frac{3}{16}$-in. rubber tube is drawn, which connects it with the leveling tube of similar size and length to the burette. It is manipulated by filling the leveling tube completely with water, opening the pinchcock on the top of the burette and filling it with water. The gas to be analyzed is sucked in and measured as with the Orsat apparatus.

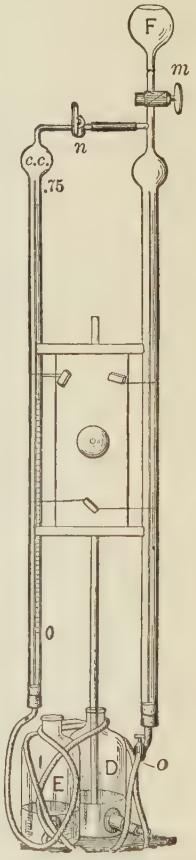


Fig. 140. Elliott Gas Apparatus.

**Orsat apparatus.** See next page.

**Separatory Funnel and Graduate.** — From the water which has flowed out, the quantity of gas can be determined.

## ANALYSIS OF GASEOUS MIXTURES

The analysis of a gaseous mixture is effected by absorbing the various constituents and observing the diminution in volume: in case the gas be unabsorbable, as for example methane ($CH_4$), it is burned and the carbon dioxide and water determined.

(*a*) *Analysis of mixtures for carbon dioxide, oxygen and carbon monoxide* (*e.g., chimney gases, producer and blast furnace gas*) can be done with any of the apparatus to be described. The Orsat or Elliott are the forms usually employed.

(*b*) *Analysis of mixtures as in* (*a*) and also containing *combustible gases* as *hydrogen and methane*, e.g., illuminating gas, requires an additional combustion pipette or absorption apparatus.

**The Orsat Apparatus. Description.** — The apparatus, Fig. 141, is enclosed in a case to permit of transportation from place to place; furthermore, the measuring-tube is jacketed with water to prevent changes of temperature affecting the gas-volume. The apparatus consists essentially of the leveling-bottle *B*, the burette *A*, the pipettes *D*, *E*, *F*, and the connecting tube. Pipette *D* is filled with potassium (or sodium) hydroxide solution (see Reagents) so that

when it is drawn up into the front arm about half an inch in depth is left in the rear arm. Pipettes *E* and *F* are similarly filled with potassium (or sodium) pyrogallate and cuprous chloride solutions respectively. These reagents require to be protected from the oxygen of the air by collapsible rubber bags. As the oxygen in the air over the reagent is absorbed, a diminution in pressure takes place render-

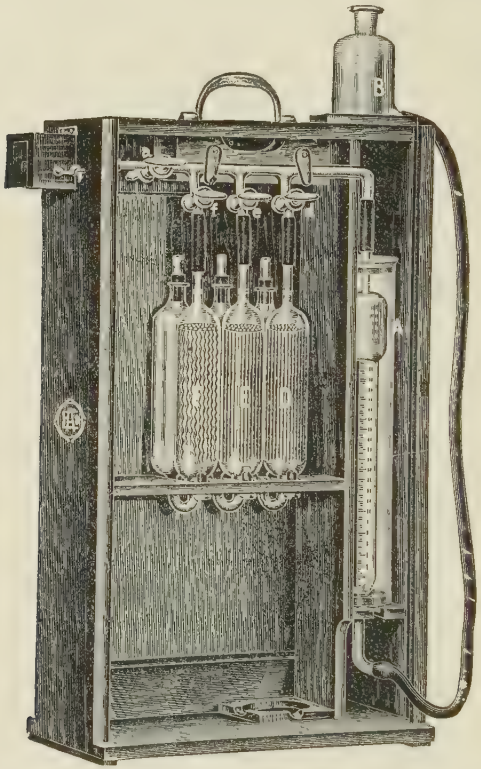


Fig. 141. Orsat Gas Apparatus.

ing it difficult to bring the reagent to the point on the stem: the obvious remedy is to remove the bag temporarily and adjust the reagent. When the apparatus is first set up, one or two blank analyses should be made, to saturate the water and reagents with the gases. For example the potassium hydroxide absorbs carbon dioxide, it also absorbs about 3 cc. of oxygen, 2 cc. of carbon monoxide and 1.5 cc. of nitrogen, by virtue of the 100 cc. of water which it contains. A change of temperature of 1° makes a change of 0.36% of the

volume of the gas: a change of pressure of 1 mm. produces 0.13% change in the volume.

**Manipulation.** — The reagents in the pipettes should be adjusted in the capillary tubes to a point on the stem about midway between the top of the pipette and the rubber connector. This is effected by opening wide the pinchcock upon the connector, the bottle being on the table, and very gradually lowering the bottle until the reagent is brought to the point above indicated. Six inches of the tubing used correspond to but 0.1 cc., so that an error of half an inch in adjustment of the reagent is without influence upon the accuracy of the result. The reagents having been thus adjusted, the burette and connecting tube are completely filled with water by opening *a* and raising the leveling-bottle. The apparatus is now ready to receive a sample of gas (or air for practice). In case a flue-gas is to be analyzed *a* is opened to allow flow into *A*. *B* is lowered and about 102 cc. of the gas drawn in; or *a* may be connected with a T-joint in the gas-stream; the burette after filling is allowed to drain one minute by the sand-glass, a pinchcock is clamped on the rubber tube, and the bottle *B* is raised to the top of the apparatus. By gradually opening the pinchcock on the rubber tubing (not shown) the water is allowed to run into the burette until the lower meniscus stands upon the 100 or 0 mark (according to the graduation of the apparatus). The gas taken is thus compressed into the space occupied by 100 cc., and by opening *a* the excess escapes. Open pinchcock and *bring the level of the water in the bottle to the same level as the water in the burette* and take the reading, which should be 100 cc. Special attention is called to this method of reading: if the bottle be raised, the gas is compressed; if lowered, it is expanded.

**Determination of Carbon Dioxide.** — The gas to be analyzed is invariably passed first into pipette *D*, containing potassium hydroxide for the absorption of carbon dioxide, by opening *d* and raising *B*. The gas displaces the reagent in the front part of the pipette, laying bare the tubes contained in it, which being covered with the reagent present a large absorptive surface to the gas; the reagent moves into the rear arm of the pipette, displacing the air over it into the flexible rubber bag which prevents its diffusion into the air. The gas is forced in and out of the pipette by raising and lowering *B*, the reagent finally brought approximately to its initial point on the stem of the pipette, the burette allowed to drain one minute, and the reading taken. The difference between this and the initial reading represents the cubic centimeters of carbon dioxide present in the gas. To be certain that all the carbon dioxide is removed, the gas should be passed a second time into *D* and the reading taken as before; these readings should agree within 0.1%.

**Determination of Oxygen.** — The residue from the absorption of carbon dioxide is passed into the second pipette, *E*, containing an alkaline solution of potassium pyrogallate, until no further absorp-

tion will take place. The difference between the reading obtained and that after the absorption of carbon dioxide, represents the number of cubic centimeters of oxygen present. Many prefer the use of stick phosphorus [1] for absorption of oxygen. The pipette *E* would require an opening at the bottom for charging with the sticks (not shown). A glass stopper closes this opening when the pipette is charged and the pipette is filled with water.

**Determination of Carbon Monoxide.** — The residue from the absorption of oxygen is passed into the third pipette, *F*, containing cuprous chloride, until no further absorption takes place; that is, in this case until readings agreeing exactly (not merely to 0.1) are obtained. The difference between the reading thus obtained and that after the absorption of oxygen, represents the number of cubic centimeters of carbonic oxide present.

**Determination of Hydrocarbons.** — The residue left after all absorptions have been made may consist, in addition to nitrogen, the principal constituent, of hydrocarbons and hydrogen.

**Accuracy.** — The apparatus gives results accurate to 0.2 of 1%, hence figures obtained by division to 0.01 should not be reported.

**Time Required.** — About twenty minutes are required for an analysis; two may be made in twenty-five minutes, using two sets of apparatus.

Notes. — The method of adjusting the reagents is the only one which has been found satisfactory: if the bottle be placed at a lower level and an attempt made to shut the pinchcock upon the connector at the proper time, it will almost invariably result in failure.

The process of obtaining 100 cc. of gas is exactly analogous to filling a measure heaping full of grain and striking off the excess with a straightedge; it saves arithmetical work, as cubic centimeters read off represent per cent directly.

It often happens when *d* is opened, *a* being closed, that the reagent *D* drops due not to a leak, as is usually supposed, but to the weight of the column of the reagent expanding the gas.

The object of the rubber bags is to prevent the access of air to the reagents, those in *E* and *F* absorbing oxygen with great avidity, and hence if freely exposed to the air would soon become useless.

Carbon dioxide is always the first gas to be removed from a gaseous mixture. In the case of air the percentage is so small, 0.08 to 0.1, as scarcely to be seen with this apparatus. It is important to use the reagents in the order given; if by mistake the gas be passed into the second pipette, it will absorb not only oxygen, for which it is intended, but also carbon dioxide; similarly if the gas be passed into the third pipette, it will absorb not only carbonic oxide, but also oxygen as well.

[1] Sticks about 5-6 inches long (the length of the pipette bulb) and approximately 3/16 to 1/4 inch in diameter.

In case any potassium hydroxide or pyrogallate be sucked over into the tube and the burette $A$, the analysis is not spoiled, but may be proceeded with by connecting with water at $a$, opening this cock, and allowing the water to wash the tubes out thoroughly. The addition of a little hydrochloric acid to the water in the bottle $B$ will neutralize the hydroxide or pyrogallate, and the washing may be postponed until convenient.

After each analysis the number of cubic centimeters of oxygen and carbonic oxide should be set down upon the ground-glass slip provided for the purpose. By adding these numbers and subtracting their sum from the absorption capacity of each reagent, the condition of the apparatus is known at any time, and the reagent can be renewed in season to prevent incorrect analyses.

## CHIMNEY AND FLUE GASES

Here the object is to keep the carbonic acid ($CO_2$) as high as possible, and to avoid the formation of carbon monoxide: in large plants every additional per cent of carbonic acid means the saving of tons of coal. Savings of 20 to 33% by the use of gas analysis alone, have frequently come to the writer's notice. A satisfactory procedure is to post in the fire-room the percentage of carbonic acid obtained by each stoker, and stimulate a rivalry among the men — a bonus in the pay envelope is also effective. The determinations to be made are:

**Analysis of Chimney Gases.** — Determination of carbon dioxide, oxygen, carbon monoxide, nitrogen, and in some cases hydrocarbons. For this purpose the Orsat apparatus is widely employed: the hydrocarbons may be determined by the Hempel apparatus.

Usually a few determinations of carbonic acid will suffice, but for regular work the installation of some form of registering carbonic acid indicator should be installed.

**Carbonic Acid Indicators.** — These usually depend upon the principle of collecting 100 cc. of the gas, causing it to pass through a suitable absorber and collecting the residue in a bell which floats to a greater or less height according to the residual volume. The fluctuations of this bell are recorded after the usual manner of self-registering barometers or thermometers: the usual time for this analysis and record is five minutes.

**The Determination of Temperature.** — This is done by inserting a thermometer, mounted in a metal tube, on the chimney side of the gas sampling tube. These resemble those used for determining steam temperatures or for "running" varnish. It should register to 360° and, under certain circumstances, one showing 550° may be desirable. A chemical thermometer with long stem may also be employed; it should never be inserted naked into the flue — as a sudden hot blast may break it — but always in a tube of cotton-seed oil or sea sand. These thermometers should be tested for accuracy by comparison with a standard, in a carefully stirred oil bath. The standard should be kept exclusively for the purpose and be allowed to stay in the bath until cool. Sudden cooling of a thermometer changes the zero point.

Electric pyrometers are also of course available for these measurements. An error of five degrees (5°) in the reading of the thermometer affects the final result by about 20 calories.

In case none of these appliances be at hand, the maximum temperature can be determined by utilizing the melting-points of certain pure salts or metals; as tin 232°, bismuth 270°, cadmium 302°, lead 327°, zinc 419°, cadmium chloride 541°, antimony 630°, etc. These can be suspended in the chimney in small covered cast-iron boxes.

**Composition of the Coal.** — This is determined by the usual methods of organic combustion and is required only for very accurate work.

Calculation:

*a.* Heat passing up chimney;

*b.* Pounds of air per pound of coal.

(*a*) *Heat Passing up Chimney.* — The accurate calculation resolves itself into finding what volume of gas of the composition determined by analysis would be produced by a kilo of the coal used, and whose analysis is known. The temperature of the escaping chimney gases being also known, and their specific heat, the quantity of heat they carry off can be calculated: this divided by the calorific power of the coal gives the per cent of heat lost in the chimney gases.

The formula of Shields.

$$\text{Per cent heat lost} = \frac{\text{Per cent carbon in coal}}{\text{Heating value of coal}} \times \frac{200 + \text{per cent } CO_2}{\text{Per cent } CO_2 + \text{per cent CO}} \times \text{rise in temperature in °C.} \times 0.2864,$$

gives results usually 0.5% low, as no cognizance has been taken of the water vapor.

Another formula in which only the carbon dioxide and its temperature enters was proposed by Bunte and gives close results.

For every per cent of carbonic acid present 43.43 calories per cubic meter of flue gases have been developed = $W$; $C$ = specific heat of the flue gases per cubic meter; then $W/C$ represents the initial temperature (which is never attained) the ratio of which to the actual exit temperature of the flue gases shows the heat lost. If $T$ = this initial temperature and $t$ the rise of temperature of the flue gases, then $t/T$ represents the heat lost in the chimney gases.

The following table gives the data for the calculation for both pure carbon and coal of average value:

| Per Cent of $CO_2$ in Chimney Gas | Specific Heat of Chimney Gas | Initial Temperature, $W/C$. Degrees C. | | |
|---|---|---|---|---|
| | | For Carbon = T | For Coal = T | Diff. for 0.1% $CO_2$ |
| 1 | 0.308 | 141 | 167 | 16 |
| 2 | 0.310 | 280 | 331 | 16 |
| 3 | 0.311 | 419 | 493 | 16 |
| 4 | 0.312 | 557 | 652 | 15 |
| 5 | 0.313 | 694 | 808 | 15 |
| 6 | 0.314 | 830 | 961 | 15 |
| 7 | 0.315 | 962 | 1112 | 15 |
| 8 | 0.316 | 1096 | 1261 | 15 |
| 9 | 0.318 | 1229 | 1407 | 14 |
| 10 | 0.319 | 1360 | 1550 | 14 |
| 11 | 0.320 | 1490 | 1692 | 14 |
| 12 | 0.322 | 1620 | 1830 | 14 |
| 13 | 0.323 | 1750 | 1968 | 13 |
| 14 | 0.324 | 1880 | 2102 | 13 |
| 15 | 0.324 | 2005 | 2237 | 13 |
| 16 | 0.325 | 2130 | 2366 | |

If there were 11.5% carbonic acid, the initial temperature $T$ would be 1762°; the rise of temperature in the chimney gases is 250°, the loss is $\frac{250}{1762}$ or 14.2%. The accurate calculation gives 14.1.

The following table shows roughly the excess of air, and per cent of heat lost in the chimney gases, their temperature being 518° F.

| Per cent $CO_2$... | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Vol. air more than theory = 1.0..... | 9.5 | 6.3 | 4.7 | 3.8 | 3.2 | 2.7 | 2.4 | 2.1 | 1.9 | 1.7 | 1.6 | 1.5 | 1.4 | 1.3 |
| Per cent loss of heat ..... | 90 | 60 | 45 | 36 | 30 | 26 | 23 | 20 | 18 | 16 | 15 | 14 | 13 | 12 |

If the oxygen be from 1.5% to 2% with the temperature of escaping gases at 400–500° F., the fires are too thick; if it be more than 8% they are too thin.

(*b*) *Pounds of Air per Pound of Coal.* — This can be determined by calculating the ratio of carbon to oxygen in the carbon monoxide and oxygen of the chimney gases, or by the formula of Shields.

$$\text{Pounds of air per pound of coal} = 2.31 \frac{\text{Per cent of carbon in coal}}{\text{Per cent } CO_2 + \text{per cent } CO}.$$

*Loss Due to Carbonic Oxide.* — For every gram of carbon burned to carbonic oxide there is a loss of 5.66 calories.

**Smoke.** — For the determination of the amount of smoke in the chimney gases, use may be made of the Ringelmann smoke scale. This consists of a series of rectangles $\frac{3}{4}$ in. × $\frac{1}{2}$ in. filled with cross-hatching lines a greater or less distance apart, with which the density of the smoke can be compared. Or the Eddy smoke recorder may be employed; this consists of a tube of standard length through which the smoke gases are drawn. A standard electric light is fixed at one end of the tube and viewed through the smoke; its density is measured by the extent to which the light is obscured.

## PRODUCER AND FUEL GASES. BLAST-FURNACE GAS.

Here the object is the reverse of that in the chimney gases, to keep the percentage of carbon monoxide as high as possible and, for gas-engine purposes, the per cent of hydrogen constant.

The determinations made are the same as in chimney gas — $CO_2$, O, CO, N, and oftentimes hydrogen and hydrocarbons; the quantity of *dust* is sometimes important. The heating value is determined by the Junkers calorimeter, although other types of calorimeters may be used such as the Sargent, Doherty, Boys and Simmance-Abady. Details of the manipulation of the Junkers apparatus may be found in the author's work, Vol. 2 of Standard Methods of Chemical Analysis. An approximate value may be obtained from the analysis of the gas, by multiplying the percentages of constituents by their calorific power in B.t.u. per cubic foot and dividing the sum of these values by 100. The following values may be taken: hydrogen = 345, carbon monoxide = 341, methane = 1065, illuminants = 2000. The efficiency of conversion would be found by measuring the number of cubic feet of gas made per ton of coal gasified; the calorific power of each (gas and coal) being known, their quotient represents the efficiency. The heat contained in the gas due to its sensible heat, found after the manner of calculating the loss in chimney gases (i.e., volume gas × weight × rise of temperature × specific heat) is to be added to this for accurate work.

## ELECTROLYTIC GASES

Gases from electrolytic chlorine, hydrogen and oxygen generators. The following are to be sought for:

(*a*) Chlorine, (*b*) oxygen, (*c*) carbon dioxide, (*d*) carbon monoxide, (*e*) hydrogen.

**(a) Chlorine.** — Hempel recommends measuring the gas quickly in his burette over water and then sucking in 5 cc. of 50% potassium iodide solution through the capillary and shaking; the diminution in volume gives the chlorine.

**The other gases** are determined in the usual way. As phosphorus cannot be used for pure oxygen, a specially prepared potassium pyrogallate is employed; cuprous chloride or ammoniacal cuprous carbonate in the absence of carbon monoxide is very satisfactory. See Reagents.

## MINE GASES

The gases sought are those found in illuminating gas. For small quantities of methane the apparatus of Haldane, modified and described by Burrell and Seibert[1] should be used. This is practically an Orsat, using mercury as the confining liquid and with a compensating tube and grisoumeter for burning the methane.

For determination of **methane** alone, the apparatus of Shaw[2] may be recommended. This determines first the per cent of illuminating gas necessary to make an explosion of definite strength with ordinary air; when this has been done, mine air is used in place of the ordinary air and a smaller percentage of illuminating is required — smaller by the amount of combustible gas in the mine air. The strength of the explosion is measured by noting by the ear the force with which the plunger is driven out from the explosion cylinder against a bell.

In case this apparatus be not at hand, Brunck's method can be employed. This consists in burning the methane in a 2 liter Erlenmeyer flask by means of an electrically heated platinum spiral. The flask carrying the spiral in the stopper is sunk inverted in a vessel of water and the current allowed to pass for half an hour, which is sufficient to burn the methane. It is then cooled and 25 cc. of $BaO_2H_2$ (1 cc. = 1 cc. of $CO_2$) added, time allowed for absorption of the carbon dioxide and the excess of $BaO_2H_2$ determined, and the quantity of methane calculated.

Clowes and Redwood have worked out a method for the detection of inflammable gas in air, employing the "flame cap." When an inflammable atmosphere is brought in contact with a candle or better a hydrogen flame, the gas burns, forming a "cap," like the colorless flame above the blue cone in a Bunsen burner: the length of the flame is a measure of the percentage of gas, and as little as 0.1% is visible using the hydrogen flame.

**Carbon Monoxide.** — Besides combustible gases or "fire damp," it is sometimes necessary to get an idea of the amount of carbon monoxide ("white damp") in the mine air after an explosion or in the "after damp"; chemical methods being too slow, use is made of the behavior of birds and mice when exposed to such an atmosphere. To this end they are carried in cages by the rescuing party and their behavior noticed. Canaries show distress in an atmosphere containing 0.15% of CO in five to twelve minutes, or with 0.20% in half this time: Mice are less sensitive, and men may display distress when carbon monoxide is as little as 0.1%, whereas animals may be unaffected. In case either is overcome by the gas, resuscitation can be effected by bringing them out into the open air again. Repeated exposure of the gas would seem to be without influence.

[1] Bull. 42, U. S. Bureau of Mines, 17, 42, 1913; also Technical Paper 39, 13.
[2] Berichte, *27*, 692.

## ATMOSPHERIC AIR

(*a*) Moisture; (*b*) Carbon dioxide; (*c*) Ozone; (*d*) Carbon monoxide; (*e*) Bacteria.

(**a**) **Moisture.** — The amount of moisture can be determined by the sling psychrometer, or wet- and dry-bulb thermometer or by

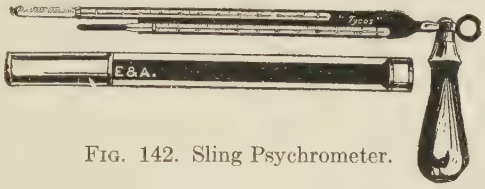



Fig. 142. Sling Psychrometer.

the hair hygrometer. The sling psychrometer is the most rapid and accurate — the wet- and dry-bulb thermometers are so arranged that they can be rapidly whirled for fifteen or twenty seconds, stopped and quickly read, the *wet* bulb first; this is repeated until closely agreeing readings are obtained. The humidity is determined in the usual manner from the meteorological tables.

The amount of moisture in the air is probably indirectly responsible for our sensations of comfort or discomfort, rather than the amount of carbon dioxide, as was formerly thought.

This moisture controls the heat loss from the body, which loss must be normal — neither too high nor too low. The greater the humidity the less the evaporation, consequently the less the cooling.

For comfort, the higher the temperature the less should be the humidity; the following shows the relation between the two:

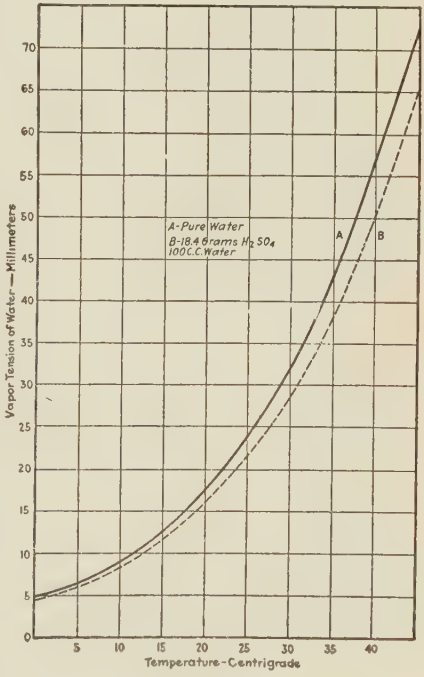



Fig. 143.

| | | | | | |
|---|---|---|---|---|---|
| Temp., °F. | 60 | 68 | 70 | 80 | 90 |
| Relative humidity, per cent | 67 | 53 | 49 | 31 | 16 |

(b) **Carbon Dioxide.** — One of the most satisfactory methods is that of Hesse. This consists in absorbing the carbon dioxide from a definite volume of air with standard barium hydroxide and determining its loss of strength.

The air is collected in heavy Erlenmeyer flasks of 100–500 or 1000 cc. capacity, or clear glass bottles; these are stoppered with doubly perforated rubber stoppers carrying glass plugs and the capacity of the flask or bottle noted to the depth of the stopper. A 10 cc. pipette and a 15 cc. glass-stoppered burette graduated in cc./10 with an 8 cm. tip, complete the outfit; a solution of 1.7 grams of barium hydroxide and chloride (20 : 1) in a liter of water, *B*, Fig. 144, and of oxalic acid 5.6325 grams per liter (1 cc. = 1 cc. of $CO_2$), with phenolphthalein 1 : 250, are required.

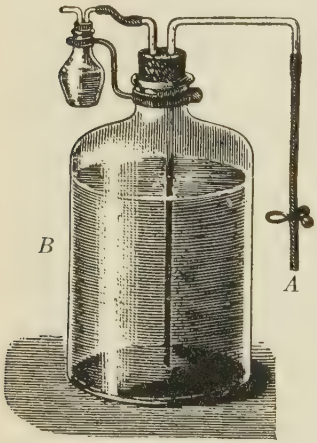


Fig. 144.

The bottles are filled with steam by exposure for three minutes and the vaselined stoppers inserted, or they may be filled with distilled water and opened in the place the air of which is to be examined.

In all this work, it should be remembered that the exhaled breath contains about 400 parts of carbon dioxide per 10,000, consequently care should be taken not to contaminate the samples, nor should they be warmed with the hand.

The 10 cc. pipette is partly filled from the tube *A*, Fig. 144, by means of the rubber connector and sucking the liquid into the pipette: it is rinsed, filled and inserted through one of the holes in the rubber stopper of the bottle, the other plug being momentarily opened. The plugs are replaced and the bottles allowed to rest on their sides, with occasional rolling, for twenty minutes. Not more than one-fifth of the solution should be used up by the carbon dioxide present.

During this time, the barium hydroxide should be standardized; to this end a few drops of phenolphthalein and a quantity of the oxalic acid almost sufficient to neutralize the hydroxide should be run into a 100 cc. Erlenmeyer flask from the burette; this should be passed through the doubly perforated stopper; 10 cc. of the barium hydroxide solution are run into the flask as above described, and also the oxalic acid until a pink color appears.

Phenolphthalein is added to the bottles containing the samples, the oxalic acid burette inserted through the stopper and the excess of barium hydroxide titrated.

The barometric pressure and temperature in the laboratory are noted and the volume of the bottle less 10 cc. ($BaO_2H_2$) calculated to standard conditions; the difference in the titer of the barium hydroxide solution gives the volume of carbon dioxide in the bottle; this is calculated into parts per 10,000.

Other methods for this determination are more strictly gasometric, measuring the diminution in volume by absorption: Benedict used Sonden's, and Anderson recommends a shortened form of the Pettersson-Palmquist apparatus.

This may be described as an Orsat apparatus using mercury instead of water and with a 25 cc. burette the lower part of which is graduated to 0.0025 cc.; this is connected to a pipette of potassium hydroxide, a delicate manometer and compensating tube. The apparatus is delicate and rapid, but requires a skilled operator to manipulate it.

The amount of carbon dioxide in the outdoor air in the city is about 3.1 parts per 10,000, in the house, 3.7–3.9; with 6–7 parts in a room, the ventilation may be considered as excellent, with 10 parts as about the upper limit. In some theaters which were lighted by gas it has approached 50 parts.

**Oxygen.** — 100 cc. of air are drawn into the Orsat apparatus, and the oxygen is absorbed either by phosphorus or by pyrogallate of potassium. The Hempel tube may be used in place of the Orsat and absorptions made in separate pipettes.

(c) **Ozone.** *Iodide Method of Schönbein.* — The method depends upon the reaction.

$$2KI + O_3 + H_2O = I_2 + O_2 + 2KOH.$$

**Procedure.** — A glass bulb of 300 cc. to 400 cc. capacity (the exact capacity being determined by weighing empty, then full of water) with two tubes at opposite sides, closed by stopcocks, one of which is a three-way cock, is filled with water. The ozone tested is introduced into the vessel, displacing the water. The gas is brought to atmospheric pressure by quickly opening and closing one of the cocks. A solution of 2N potassium iodide is introduced in excess of that required, through the three-way cock by means of a second bulb connected by a rubber tube to the vessel, after displacing the air in the rubber connection through the cock. The mixture is well shaken and allowed to stand half an hour. The contents of the bulb are washed out with additional iodide solution, followed by distilled water and the liberated iodine titrated with standard thiosulphate.

$$1 \text{ cc. of } N/10\ Na_2S_2O_3 = 0.0024 \text{ g. of } O_3.$$

(d) **Sulphur dioxide** in the atmosphere. See chapter on Sulphur, page 557.

(e) **Carbon Monoxide.** — The qualitative detection is most certainly effected by the blood test; to this end the gas is drawn through a solution of blood contained in a Wolff, Fig. 145, or similar absorption tube and examined for its absorption spectrum. The blood solution is made by mixing ox blood which has been defibrinated by whipping, with an equal quantity of a cold saturated solution of borax; this can be kept (as a side-shelf reagent) in the laboratory for months. This solution is diluted with 19 volumes of water, giving a solution of blood of 1 in 40 which is placed in the absorption tube. The air is drawn through it at a rate of 3 liters per hour, requiring 10 liters in some cases; the solution is put in a thin flat-sided bottle and spectroscopically examined.

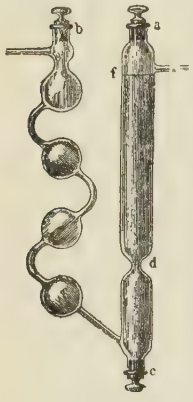


FIG. 145.

Pure diluted blood, Fig. 146, shows two dark absorption bands, spectrum 2, between the *D* and *E* line; these are welded into one broad band by reducing agents such as $NH_4SH$, spectrum 4; blood which has absorbed carbon monoxide shows two broader bands in the same place, spectrum 3, which are unaffected by reducing agents. The quantitative determination depends upon the equation,

$$5CO + I_2O_5 = 5CO_2 + I_2.$$

This has been studied by Kinnicutt and Sanford [1] and recently by Morgan and McWhorter [2] and by the writer. The process consists in sucking the air through the iodine pentoxide contained in a U-tube heated in a cottonseed oil or glycerin bath to 150° C., passing the iodine into potassium iodide solution and then absorbing the carbon dioxide in standard barium hydroxide. Both the iodine and barium hydroxide solutions are titrated. The last two investigators call particular attention to the ease with which iodine pentoxide at 150° is decomposed by organic matter, particularly stopcock grease; the pentoxide should be sealed into the U-tube, as glass stopcocks cannot be used. The writer can substantiate this statement, and would suggest further that the U-tube be chemically cleaned with cleaning solution ($Na_2Cr_2O_7 + H_2SO_4$) before filling with $I_2O_5$, as well as the tubes through which the gas

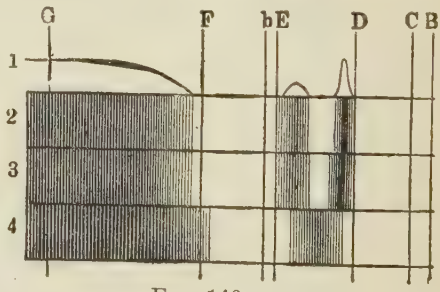


FIG. 146.

[1] J. Am. Chem. Soc., **22**, 14, 1900. [2] Ibid., **29**, 1589, 1907.

is sucked before reaching the U-tube; rubber connections should, if possible, be avoided, and the tubing should have been cleansed by warming with dilute soda lye and washing. The U-tube should be drawn down into the same size as the connecting glass tubing and the two butted closely together in the cleansed rubber connector.

The iodine is titrated with N/1000 thiosulphate and every 2.27 mg. of iodine corresponds to 1 cc. of carbon monoxide under standard conditions; the carbon dioxide is absorbed in the hydroxide contained in a long test-tube 24 × 2.5 cm. and titrated with oxalic acid (1.1265 grams crystallized acid to 1 liter) using phenolphthalein; 5 cc. of the acid are equivalent to 1 cc. of carbon dioxide.

Haldane[1] states that as little as 0.01% of carbon monoxide can be determined colorimetrically by absorbing in diluted blood and comparing it with standard carmine solution; carbon monoxide turns the brownish yellow color of the blood to pink.

(f) **Bacteria.** — See "Standard Methods for Bacterial Examination of Air." Am. J. Pub. Health, 6, No. 3, 1910, also "Standard Methods of Chemical Analysis," Scott, pages 1442 to 1468.

Calorific Power of Various Gases in British Thermal Units per Cubic Foot

| Name | Symbol | 60° F. Initial | 32° F. Initial 32° F. Final | Ignition Point °F. |
|---|---|---|---|---|
| Hydrogen | $H_2$ | 326.2 | 345.4 | 1085 |
| Carbonic oxide | CO | 323.5 | 341.2 | 1200 |
| Methane | $CH_4$ | 1009.2 | 1065.0 | 1230 |
| Illuminants | .... | ..... | 2000.0 | .... |
| Ethane | $C_2H_6$ | 1764.4 | 1861.0 | 1140 |
| Propane | $C_3H_8$ | 2521 | 2657.0 | 1015 |
| Butane | $C_4H_{10}$ | 3274 | 3441.0 | .... |
| Pentane | $C_5H_{12}$ | ..... | 4255.0 | .... |
| Hexane | $C_6H_{14}$ | ..... | 5017.0 | 1400 |
| Ethylene | $C_2H_4$ | 1588 | 1674.0 | 1010 |
| Propylene | $C_3H_6$ | 2347.2 | 2509.0 | 940 |
| Benzene | $C_6H_6$ | 3807.4 | 4012.0 | .... |
| Acetylene | $C_2H_2$ | 1476.7 | 1477.0 | 788 |

| | | | |
|---|---|---|---|
| 1 pound | = 453.59 grams | 1 calorie | = 3.969 B.t.u. |
| 1 cubic inch | = 16.39 cc. | 1 cubic meter | = 35.31 cu. ft. |
| 1 cubic foot | = 28.315 liters | | |
| 1 B.t.u. per cu. ft. | = 8.89 calorie per cubic meter | 1 calorie per cu. meter | = 0.1124 B.t.u. per cu. ft. |
| 1 in. $H_2O$ pressure | = 1.87 mm. Hg pressure | 1 mm. Hg pressure | = 0.535 in. $H_2O$ pressure |

[1] Clowes, op. cit., 138.

### Acetylene

Absorbents—Fuming sulphuric acid. Ammoniacal cuprous chloride produces a red color. Used as qualitative test.

### Ethylene (in presence of Acetylene)

Absorbent—Fuming sulphuric acid absorbs Acetylene and Ethylene. Cold bromine or iodine solution, Ethylene not attacked. Hence determined both by $H_2SO_4 + SO_3$ and Ethylene by Br. Difference equal Acetylene.

### Benzene

Absorbent—Fuming sulphuric acid. Bromine water + Br. $CO_2$ is first absorbed by KOH (saturated with benzene vapor), then benzene in fuming sulphuric acid.

This chapter was contributed by A. H. Gill, Professor of Technical Analysis, Massachusetts Institute of Technology.

## PREPARATION OF REAGENTS

This chapter includes a list of reagents generally used in the analytical laboratory. Certain special reagents having a limited use are given in the body of the text under the subject with which they are concerned. The alphabetical arrangement will be found convenient for reference. The term percent is used for convenience and does not represent true percent but rather the grams of reagent per 100 cc. of solution.

Common Laboratory Desk or Shelf Reagents

| Reagent Name | Per Cent | Vol. R. | Vol. $H_2O$ | Res. sp. gr. | Approx. N. | Gm. per cc. |
|---|---|---|---|---|---|---|
| Acetic a. glacial | 100 | ..... | ..... | 1.06 | 17 N | 1.06 g. |
| Acetic a. | 80 | ..... | ..... | 1.07 | 15 N | 0.84 g. |
| Acetic a. dil. | 28 | 1 | 2 | 1.04 | 5 N | 0.28 g. |
| Hydrochloric a. conc. | 40 | ..... | ..... | 1.20 | 13 N | 0.48 g. |
| Hydrochloric a. dil. | 16 | 1 | 1.5 | 1.08 | 5 N | 0.19 g. |
| Nitric a. conc. | 96 | ..... | ..... | 1.50 | 23 N | 1.43 g. |
| Nitric a. commer. | 70 | ..... | ..... | 1.42 | 16 N | 1.00 g. |
| Nitric a. dil. | 23 | 1 | 2 | 1.14 | 5 N | 0.31 g. |
| Sulphuric a. conc. | 95 | ..... | ..... | 1.84 | 36 N | 1.77 g. |
| Sulphuric a. dil. | 14 | 1 | 6 | 1.09 | 5 N | 0.25 g. |
| Ammonium hyd. conc. | 28 | ..... | ..... | 0.90 | 15 N | 0.26 g. |
| Ammonium hyd. dil. | 9 | 1 | 2 | 0.96 | 5 N | 0.08 g. |
| Sodium hyd. | 40 | ..... | ..... | 1.44 | 14 N | 0.58 g. |
| Sodium hyd. dil. | 14 | 1 | 2 | 1.07 | 5 N | 0.20 g. |

R = strong reagent. Res. = resulting. N = Normal. Gm. per cc. = grams of 10% reagent.

### Reagents Used for Precipitations and Volumetric Determinations

Volumetric reagents should be standardized at 20° C. if possible. The temperature at which the standardization is made should be noted on the container as the strength of the reagent per cc. will vary with a change of temperature, the concentration increasing with contraction at a lower temperature, and expansion causing decrease with a rise in temperature. It is not advisable to attempt to make the reagent exactly a normal equivalent as the strength may change slightly from this factor. It is necessary to establish the exact factor of the solution, however, by careful standardization. The "factor" is the ratio between a given number of cc. of the solution in question and the number of cc. of a theoretically correct

solution. For example, if 50 cc. of the reagent were found to be equivalent to 55 cc. of a theoretically normal solution, the normality factor of the reagent in question would be $55 \div 50 = 1.1$ N. and all titrations would have to be multiplied by this factor to obtain the cc. in terms of a normal solution.

Normalities are expressed either by a figure before N or after it, thus 0.2 N or N/5 = fifth normal. 0.1 N or N/10 = tenth normal. 0.5 N or N/2 = half normal. .02 N or N/50 = fiftieth normal, etc.

## PREPARATION OF REAGENTS

**Acetic Acid, Glacial.** — C.P., 99.5% pure. The determination of its strength should be made by titration and not by specific gravity, as the 98% and 80% acid have the same specific gravity, 1.067. The determination of the melting-point gives results equally good with those obtained by titration and requires less time. It is made after the manner of the "titer test" for acids, the tube being half filled, chilled to 10° to 11° C., and further chilled by placing the outside bottle in ice-water; the temperature of the super-cooled acid rises to its melting-point, where it remains stationary for some time. The melting-points of acids of various strengths are as follows:

100%, 16.75° C.; 99.5%, 15.65°; 99%, 14.8°.

**Alcohol.** — Commercial "Cologne Spirits." For the preparation of alcohol free from aldehyde for alcoholic potash, cologne spirits are treated with silver oxide as follows: $1\frac{1}{2}$ grams of silver nitrate are dissolved in 3 cc. of water, added to 1 liter of alcohol and thoroughly shaken; 3 grams of potassium hydrate are dissolved in 15 cc. of warm alcohol and, after cooling, added to the alcoholic silver nitrate and thoroughly shaken again, best in a tall bottle or cylinder. The silver oxide is allowed to settle, the clear liquid siphoned off and distilled, a few bits of pumice, prepared by igniting and immediately quenching under water, being added to prevent bumping. Alcohol for use in the free acid determination is prepared by placing 10 to 15 grams of dry sodium carbonate in the reagent bottle, taking care to filter it before use.

**Alcohol, Amyl.** — C.P.

**Alcohol Potash Solution.** — See potassium hydroxide.

**Alizarin S Test.** — The reagent used is a 0.1% filtered solution of commercial alizarin S, the sodium salt of alizarin monosulphonic acid (yellow with acids, purple with alkalies).

**Alkaline Tartrate Solution.** — See Tartrate Solution.

**Ammonium Acetate.** — 70% solution. Use the salt or cautiously add 1000 cc. of ammonium hydroxide to 1200 cc. of glacial acetic acid.

**Ammonium Carbonate.** — 250 grams of the salt per liter. Add 100 cc. of strong ammonium hydroxide. The solution contains approximately 22% of $(NH_4)_2CO_3.NH_4CO_2NH_2$.

**Ammonium Chloride.** — 10% solution, 100 grams of $NH_4Cl$ per liter.

**Ammonium Chloride** *Solution Standard.* — Dissolve 3.82 grams of ammonium chloride in 1 liter of distilled water. Dilute 10 cc. of this to 1 liter with ammonia-free water. 1 cc. = 0.00001 gram of nitrogen. Used in water analysis.

**Ammonium Molybdate** *Reagent Standard.* — 4.75 grams of the salt are dissolved in water and made up to 1 liter. One cc. with a half gram sample is equal approximately to 1% of Pb. Standard in lead determination.

**Ammonium Molybdate.** — One hundred grams of pure molybdic acid are thoroughly mixed with 400 cc. of cold distilled water and 80 cc. of strong ammonia (sp.gr. 0.90) added. When the solution is complete it is poured slowly and with constant stirring into a mixture of 400 cc. of strong nitric acid (sp.gr. 1.42) and 600 cc. of distilled water. This order of procedure should be followed, as the nitric acid poured into the ammonium molybdate solution will cause the precipitation of a difficultly soluble oxide of molybdenum and necessitate filtration. Fifty milligrams (.05 gram) of microcosmic salt, dissolved in a little water are added to clarify the reagent, the precipitate agitated, then allowed to settle for twenty-four hours and the clear solution decanted through a filter into a large reagent bottle. Sixty cc. of the reagent should be used for every 0.1 gram of $P_2O_5$ present in the solution analyzed.

**Ammonium Nitrate.** — 20% solution. 200 grams of $NH_4NO_3$ per liter.

**Ammonium Oxalate.** — 4% solution. 40 grams of $(NH_4)_2C_2O_4.2H_2O$ per liter.

**Ammonium Phosphate.** — 10% solution. 100 grams of $(NH_4)_2HPO_4$ per liter. Sodium ammonium phosphate Microcosmic salt may be used in place of ammonium phosphate.

**Ammonium Sulphate.** — 25% solution. 250 grams of $(NH_4)_2SO_4$ per liter.

**Ammonium Sulphide** (Colorless). — Saturate 750 cc. of strong ammonia with hydrogen sulphide gas and add 500 cc. of strong ammonia and 1000 cc. of water.

**Ammonium Polysulphide** (Yellow). — To a solution of ammonium sulphide made according to the directions above add about 75 grams of flowers of sulphur. Shake well.

**Ammonium Thiocyanate** ("sulphocyanate"). — See Thiocyanate.

**Arsenic Standard Solution.** — One gram of resublimed arsenous acid, $As_2O_3$, is dissolved in 25 cc. of 20% sodium hydroxide solution (arsenic free) and neutralized with dilute sulphuric acid. This is diluted with fresh distilled water, to which 10 cc. of 95% $H_2SO_4$ has been added, to a volume of 1000 cc. Ten cc. of this solution is again diluted to a liter with distilled water containing acid. Finally 100 cc. of the latter solution is diluted to a liter with distilled water containing acid. One cc. of the final solution contains 0.001 milli-

gram of $As_2O_3$. Used in arsenic determinations by Gutzeit and Marsh methods.

**Arsenite.** *Tenth Normal Arsenious Acid.* — $As_2O_3$ is equivalent to $2I_2$, i.e., to 4H, hence $\frac{1}{4}$ the gram molecular weight of arsenious oxide per liter will give a normal solution: $198 \div 4 = 49.5$.

4.95 grams of pure arsenious oxide is dissolved in a little 20% sodium hydroxide solution and the excess of the alkali is neutralized with dilute sulphuric acid, using phenolphthalein indicator, the solution being just decolorized. Five hundred cc. of distilled water containing about 25 grams of sodium bicarbonate are added. If a pink color develops, this is destroyed with a few drops of weak sulphuric acid. The solution is now made to volume, 1000 cc. The reagent is standardized against a measured amount of pure iodine. The oxide may be dissolved directly in sodium bicarbonate solution. For iodine titrations. A standard reducing agent.

Note. Commercial arsenious oxide is purified by dissolving in hot hydrochloric acid, filtering the hot saturated solution, cooling, decanting off the mother liquor, washing the deposited oxide with water, drying and finally subliming.

**Standard Antimony Solution.** — A stock solution is made up by weighing out 0.553 gms. of $KSbOC_4H_4O_6$ which is dissolved in distilled water and made up to 2000 cc. which represents 1 cc. = .0001 grm. of Sb.

From the above stock solution take 100 cc. and make up to 1000 cc.; this solution now equals – 1 cc. = .00001 grm. of Sb, which is used for making the standard stains and introducing into checks. For standard antimony stains.

**Barium Chloride.** — A 10% solution. 100 grams of $BaCl_2.2H_2O$ per liter.

**Barium Chloride,** anhydrous, 5% solution; or crystals, 6% solution. Reagent used for sulphur determinations.

**Barium Hydroxide.** — 5% solution. 50 grams of $Ba(OH)_2.8H_2O$ per liter.

**Alpha Benzildioxime.** — This may be prepared by boiling 10 grams of benzil (not necessarily pure) with 8 to 10 grams of hydroxylamine hydrochloride in methyl alcohol solution. After boiling for three hours the precipitate is filtered off and dried, washed with hot water and then with a small amount of 50% alcohol, and dried. This dried precipitate consists of pure benzildioxime (m.p. 237° C.). A further yield may be obtained by boiling the filtrate with hydroxylamine hydrochloride. The reagent is prepared by dissolving 0.2 gram of the salt per liter of alcohol to which is added ammonium hydroxide to make 5% solution, sp.gr. 0.96 (50 cc. per liter). Reagent used in the determination of nickel.

**Benzidine hydrochloride** is prepared by taking 6.7 grams of the free base, or the corresponding amount of the hydrochloride and

mixing into a paste with 20 cc. of water in a mortar. Twenty cc. of hydrochloric acid (sp.gr. 1.12) are added and the mixture diluted to exactly 1000 cc. One cc. of this solution corresponds to 0.00357 gram of $H_2SO_4$. The solution has a brown color. Brown flakes are likely to separate out on standing, but these do no harm.

Reagent used in the determination of sulphur.

**Bromine.** — The commercial article; also a N/3 solution, made by dissolving 26.6 grams of bromine in 1 liter of carbon tetrachloride.

**Bromine — Potassium Bromide Solution.** — 320 grams of potassium bromide are dissolved in just sufficient water to cause solution and mixed with 200 cc. of bromine, the bromine being poured into the saturated bromide solution. After mixing well the solution is diluted to 2000 cc. Used for sulphur determinations.

**Bromine — Carbon Tetrachloride Solution.** — Carbon tetrachloride saturated with bromine. Used for sulphur determination.

**Bismuth Standard Solution.** — One gram of metallic bismuth is dissolved in the least amount of dilute nitric acid (1:1) that is necessary to keep it in solution and diluted to 1000 cc. in a graduated flask. One hundred cc. of this solution is diluted to 1000 cc. One cc. of this diluted solution contains 0.0001 gram of bismuth.

**Calcium Chloride.** — 10% solution. 100 grams of $CaCl_2.6H_2O$ per liter.

**Acid Calcium Chloride Solution.** — Saturate with calcium chloride a mixture of 90 parts of water and 10 parts of concentrated hydrochloric acid (specific gravity 1.2).

**Calcium Hydroxide** (Lime Water). — A saturated water solution of $Ca(OH)_2$. Keep tightly stoppered. Decant or filter before use.

**Cinchonine Solution.** — Cinchonine solution is made by dissolving 100 grams of the alkaloid in dilute HCl (1 part acid to 3 of water) and diluting to 1000 cc. with HCl of the same strength.

**Cinchonine Wash Solution.** — 30 cc. of Cinchonine solution, 30 cc. of strong HCl diluted to 1000 cc. Used in tungsten determinations.

**Cinchonine Potassium Iodide Solution.** — Ten grams of cinchonine are dissolved by treating with the least amount of nitric acid that is necessary to form a viscous mass and taking up with about 100 cc. of water. The acid is added a drop at a time, as an excess must be avoided. Twenty grams of potassium iodide are dissolved separately and cinchonine solution added. The resulting mixture is diluted with water to 1000 cc. After allowing the reagent to stand forty-eight hours, any precipitate formed is filtered off and the clear product is ready for use. The reagent preserved in a glass-stoppered bottle keeps indefinitely. It should be filtered free of suspended matter before use.

**Copper Sulphate – Alkaline Tartrate Solution.** — See Fehling's solution.

**Citric Acid.** — One part of acid in of 3 parts water. One hundred cc. of nitric acid should be added to each liter to prevent mould growth.

**Citrate of Ammonia.** — 25 grams of the salt per 50 cc. of water.

**Copper Solution Standard.** — One gram of purest electrolytic copper is dissolved in 20 cc. of dilute nitric acid, sp.gr. 1.2, and the solution diluted to 1000 cc. For standardizing the thiosulphate to be used with high-grade copper ores, crude copper, blister copper, etc., a copper solution containing ten times the above amount of metallic copper is prepared. Standard in the iodide determination of copper.

**Caustic.** — Standard solution. See sodium hydroxide.

**Devarda's Alloy.** — Forty-five parts of aluminum, 50 parts of copper and 5 parts of zinc. The aluminum is heated in a Hessian crucible in a furnace until the aluminum begins to melt, copper is now added in small portions until liquefied and zinc now plunged into the molten mass. The mix is heated for a few moments, covered and then stirred with an iron rod, allowed to cool slowly with the cover on and the crystallized mass pulverized.

**Dimethylglyoxime.** — 1% solution. 1 gram of the salt per 100 cc. of ethyl alcohol. Used in nickel determinations.

**Diphenyl Carbazide Reagent.** — One-tenth of a gram of the compound is dissolved in 10 cc. of glacial acetic acid and diluted to 100 cc. with ethyl alcohol.

Diphenyl carbazide may be made by heating a mixture of 15 grams of urea with 50 grams of phenyl hydrazine four hours, finishing at 155° C. The solid product is crystallized three times with alcohol. A light straw-colored product is obtained. A white product is obtained if the urea is cut down to 5 grams, the yield, however, is only 25 per cent of that obtained by the first method and the compound possesses no advantages. Used in chromium determinations.

**Fehling's** *Solution for Determination of Sugar.* — (*a*) *Copper sulphate solution.* — 34.639 g. of crystallized copper sulphate are dissolved in water and made up to 500 cc. (*b*) *Alkaline tartrate solution.* Dissolve 173 g. of Rochelle salts and 125 g. of potassium hydroxide in water and dilute to 500 cc.

**Ferric Chloride.** — 10% solution. 100 grams of $FeCl_3.6H_2O$ per liter.

**Ferric Chloride Solution Standard.** — (10 grams of iron dissolved in 200 cc. of HCl, oxidized with $HNO_3$ and made to one liter.) 1 cc. = 0.01 g. of Fe.

**Ferric Indicator.** — Saturated solution of ferric ammonium alum. Should this not be available, $FeSO_4$ may be oxidized with nitric acid, and the solution evaporated with an excess of $H_2SO_4$ to expel the nitrous fumes. A 10% solution is desired. Five cc. of either of these reagents are taken for each titration. Used in titrating silver by Valhard's method.

**Standard Iron Solution.** — A ferric solution, the iron content of which has been determined, is diluted and divided so as to obtain 0.0004 gram of Fe. This is made up to 2 liters with water containing 200 cc. of iron-free, C.P. $H_2SO_4$. One hundred cc. of this solution,

together with 10 cc. of normal ammonium sulphocyanate solution, is used as a standard. One hundred cc. contains 0.00002 gram of Fe.

Normal sulphocyanate contains 76.1 grams of $NH_4CNS$ per liter.

Used in standardization of the reagent for the determination of iron.

**Cuprous Chloride, Acid, for Gas Analysis.** — The directions given in the various text-books being troublesome to execute, the following method, which is simpler, has been found to give equally good results: Cover the bottom of a two-liter bottle with a layer of copper oxide or "scale" $\frac{3}{8}$ in. deep, place in the bottle a number of pieces of rather stout copper wire reaching *from top to bottom*, sufficient to make a bundle an inch in diameter, and fill the bottle with common hydrochloric acid of 1.10 sp.gr. The bottle is occasionally shaken, and when the solution is colorless, or nearly so, it is poured into the half-liter reagent bottles, containing copper wire, ready for use. The space left in the stock bottle should be immediately filled with hydrochloric acid (1.10 sp.gr.).

By thus adding acid or copper wire and copper oxide when either is exhausted, a constant supply of this reagent may be kept on hand.

*The absorption capacity* of the reagent per cc. is, according to Winkler, 15 cc. of CO; according to Hempel 4 cc.

Care should be taken that the copper wire does not become entirely dissolved and that it extend from the top to the bottom of the bottle; furthermore the stopper should be kept thoroughly greased the more effectually to keep out the air, which turns the solution brown and weakens it.

**Cuprous Chloride, Ammoniacal, for Gas Analysis.** — The acid cuprous chloride is treated with ammonia until a faint odor of ammonia is perceptible; copper wire should be kept in it similarly to the acid solution. This alkaline solution has the advantage that it can be used when traces of hydrochloric acid vapors might be harmful to the subsequent determinations, as, for example, in the determination of hydrogen by absorption with palladium. It has the further advantage of not soiling mercury as does the acid reagent.

*Absorption Capacity*, 1 cc. absorbs 1 cc. of CO.

Cuprous chloride is at best a poor reagent for the absorption of carbonic oxide; to obtain the greatest accuracy where the reagent has been much used, the gas should be passed into a fresh pipette for final absorption, and the operation continued until two consecutive readings agree exactly. The compound formed by the absorption — possibly $Cu_2COCl_2$ — is very unstable, as carbonic oxide may be freed from the solution by boiling or placing it *in vacuo*; even if it be shaken up with air, the gas is given off, as shown by the increase in volume and subsequent diminution when shaken with fresh cuprous chloride.

**Hydrogen.** — Pure zinc is placed in a Kipp generator and dilute 1 : 1 sulphuric acid is added, and a few cc. of copper sulphate (10%) then added. Hydrogen is evolved by the action of the acid on zinc.

**Standard Iron Solution.** — 8.6322 grams of ferric ammonia alum is dissolved in dilute hydrochloric acid and made up to one liter. The iron is determined in 100 cc. portions by the dichromate method. One cc. will contain about 0.001 gram of Fe.

**Ferric Nitrate.** — One part of salt in 6 parts of water. It is well to add a little nitric acid to prevent hydrolysis.

**Ferrous Sulphate Standard. Reagent for Nitric Acid Determinations.** — *A. Reagent to be Used in Titration of Nitric Acid in Sulphuric Acid, Oleum, etc.* — 176.5 grams of $FeSO_4.7H_2O$ are dissolved in about 400 cc. of water, and 500 cc. of about 60% $H_2SO_4$ (1 vol. of 66° Bé. acid per 1 vol. of $H_2O$) are added with constant stirring, and the solution (cooled if necessary) made up to 1000 cc. 1 cc. will be equivalent to 0.02 ± gram of $HNO_3$, the exact value being determined by standardization.

*B. Reagent for Titration of Nitric in Phosphoric or Arsenic Acid.* — Ferrous sulphate to be used, should be made up as follows: 264.7 grams of $FeSO_4.7H_2O$ is dissolved in 500 cc. of water, 50 cc. of 66° Bé. $H_2SO_4$ (93.2%), added and the solution made up to 1000 cc. 1 cc. will be equal to approximately 0.02 gram of $HNO_3$. The exact strength is ascertained by titrating a known amount of nitric acid in phosphoric or arsenic acid upon warming to 40° or 50° C.

**Hydrochloric Acid, Arsenic-free.** — The commercial acid is treated with potassium chlorate to oxidize the arsenic to its higher form and the acid distilled. The distilling apparatus may be arranged so that constant distillation takes place, acid from a large container dropping slowly into a retort containing potassium chlorate, fresh hydrochloric acid being supplied as rapidly as the acid distills. See Fig. 147.

**Hydrochloric Acid.** — Desk reagent. See beginning of chapter.

**Hydrochloric Acid.** — Standard. Consult chapter on Acidimetry and Alkalimetry, page 666.

**Hydrogen Peroxide.** — Thirty per cent solution. If this is not available, sodium peroxide dissolved in dilute sulphuric acid will do.

**Hydrogen Sulphide.** — See page 783.

**Iodine Solution.** — Standard 0.1 N. Dissolve 20–25 grams of potassium iodide in as little water as possible. To this add 12.7 grams of resublimed iodine (theoretical amount 12.692 grams), and when dissolved make up to a liter, preferably in a dark colored bottle as the light affects the solution.

*Standardization.* — For general use standardize the iodine against 0.1 N sodium thiosulphate, or 0.1 N arsenous acid solution, taking 50 cc. of the reagent, carefully measured from a burette or pipette, adding a solution of starch and then the iodine solution until a blue color is obtained. Establish the factor for the iodine in terms of a true 0.1 solution. Note the temperature of the solution and make record on the bottle.

For tin plate analysis standardize the iodine solution against standard tin solution. It is convenient to adjust the iodine solution so that 1 cc. equals exactly .00579 gram of tin. Then, if a sample of the plate having a total surface of 8 sq. in. is taken, 1 cc. of the iodine

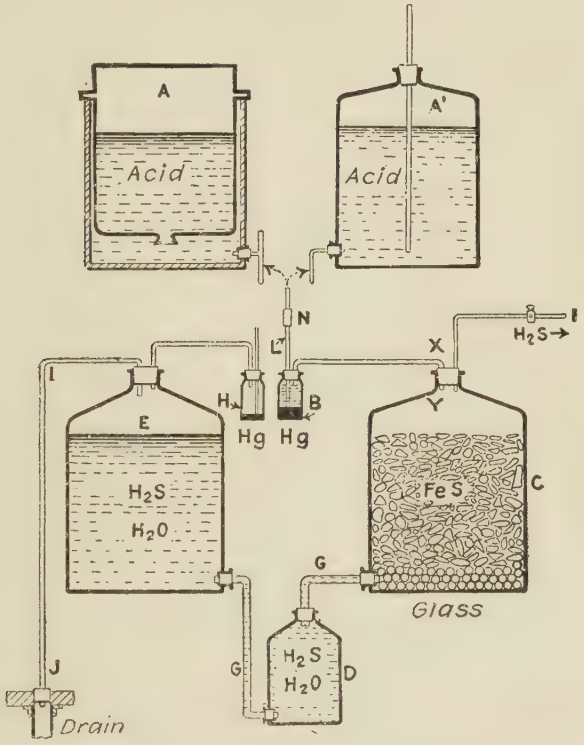



Fig. 147. Hydrogen Sulphide Gas Generating Apparatus

The apparatus is assembled with *A* empty at any convenient height greater than the desired gas pressure, above *E* and *C*. The minimum pressure of gas, in inches of water, desired at *F* is then decided upon. Six inches is satisfactory for most work. Water is added at *E* and air is allowed to escape through *F* until water just reaches the iron sulphide in *C*. *F* is then closed and *E* is filled with water. *F* is carefully opened and water is allowed to flow from *E* to *C* until the difference between the levels in the two bottles equals the desired minimum lead in inches of water. *F* is then closed; *A* is filled with dilute acid and the mercury layer in *B* is adjusted until the pressure of the acid column is just sufficient to overcome the back pressure of the mercury column in *B* and the air pressure in *C*. This is best accomplished by adding slightly more mercury than necessary and then carefully raising *L* until the dilute acid begins to drop on the sulphide. A short rubber tubing insert at *N* facilitates this operation. After the mercury layer is correctly adjusted *F* is opened and the apparatus is ready to function. No further adjustments are necessary and operation is entirely automatic. To obtain hydrogen sulphide open cock *F*.

solution is the equivalent of one-tenth of a pound per base box. Use starch as indicator.

**Lead Acetate.** — 10% solution. 100 grams of $Pb(C_2H_2O_1)_1.3H_2O$ per liter. If cloudy, clear with a few cc. of acetic acid.

**Standard Lead Solution.** — A convenient solution may be made by dissolving 0.1831 gram of lead acetate, $Pb(C_2H_3O_2)_2.3H_2O$, in 100 cc. of water, clearing any cloudiness with a few drops of acetic acid and diluting to 1000 cc. If 10 cc. of this solution are diluted to 1000 cc. each cc. will contain an equivalent of 0.000001 gram Pb.

Harcourt suggests a permanent standard made by mixing ferric, copper and cobalt salts. For example 12 grams of $FeCl_3$ together with 8 grams of $CuCl_2$ and 4 grams of $Co(NO_3)_2$ are dissolved in water, 400 cc. of hydrochloric acid added and the solution diluted to 4000 cc. 150 cc. of this solution together with 115 cc. of hydrochloric acid (1 : 2) diluted to 2000 cc. will give a shade comparable to that produced by the standard lead solution above, when treated with the sulphide reagent. The exact value per cc. may be obtained by comparison with the lead standard.

**Lead Acetate Test Paper for Removal of $H_2S$.** — Large sheets of qualitative filter paper are soaked in a dilute solution of lead acetate and dried. The paper is cut into strips $7 \times 5$ cm.

**Lead Acetate Cotton. Preparation of.** — A roll of absorbent cotton is opened and saturated with a 10% solution of lead acetate and surplus drained off, then hung on a line to dry in a warm place away from the influence of hydrogen sulphide. Do not dry in an oven. When dry place in a stoppered bottle until used.

**Magnesium Ammonium Chloride. Magnesia Mixture.** — For precipitation of ammonium magnesium phosphate, 110 grams of magnesium chloride ($MgCl_2.6H_2O$) are dissolved in a small amount of water. To this are added 280 grams of ammonium chloride and 700 cc. of ammonia (sp.gr. 0.90); the solution is now diluted to 2000 cc. with distilled water. The solution is allowed to stand several hours and then filtered into a large bottle with glass stopper. Ten cc. of the solution should be used for every 0.1 gram $P_2O_5$ present in the sample analyzed. As the reagent becomes old it will be necessary to filter off the silica that it gradually accumulates from the reagent bottle.

**Magnesia Wash Solution.** — For washing magnesium ammonium phosphate precipitate. 100 grams of $NH_4NO_3$ are dissolved in water, 335 cc. of strong $NH_4OH$ added and the solution diluted to 1000 cc.

**Manganous Sulphate Solution.** — 48 grams of manganous sulphate are dissolved in 100 cc. of distilled water.

**Mercuric Chloride.** — Saturated solution of $HgCl_2$ (60 to 100 grams per liter).

**Mercuric Chloride.** — 5% solution. 50 g. of $HgCl_2$ per liter.

**Sensitized Mercuric Chloride (or Bromide Paper).** — $20 \times 20$ in. Swedish Filter Paper No. 0 is cut into four equal squares. For use in

the large Gutzeit apparatus the paper is dipped into a 3.25% solution of mercuric chloride (mercuric bromide may be used in place of the chloride) or if it is to be used in the small Gutzeit apparatus it is dipped into a 0.35% mercuric chloride solution. (The weaker the solution, the longer and less intense will be the stain.) The paper should be of uniform thickness, otherwise there will be an irregularity in length of stain for the same amounts of arsenic. See chapter on Arsenic.

**Methyl Red Solution.** — 0.25 gram of methyl red is dissolved in 2000 cc. of 95% alcohol; 2 cc. of the indicator are used for each titration. As the indicator is sensitive to $CO_2$, all water used must first be boiled to expel carbonic acid.

**Nessler's Solution.** — Dissolve 50 grams of potassium iodide in the smallest possible quantity of cold water. Add a saturated solution of mercuric chloride until a faint show of excess is indicated. Add 400 cc. of 50% solution of potassium hydrate. After same has clarified by sedimentation, make up to 1 liter with water, allow to settle and decant. For determining $NH_3$ in water.

**Nitric Acid.** — Desk reagents. See beginning of the chapter.

**Nitric Acid** — Tenth Normal Solution. — The acid is standardized against the caustic solution and should be of such strength that 1 cc. of $HNO_3$ is equal to 1 cc. of NaOH. Phenolphthalein indicator is used. Approximately 6.7 cc. of 95% $HNO_3$ diluted to 1000 cc. = N/10 $HNO_3$ solution.

**Nitric Acid Standard — Ferrous Sulphate Method for Nitrates.** — *Standardization of the Acid.* — 11.6 grams of standard potassium nitrate, equivalent to about 9.6 grams of $NaNO_3$, are dissolved and made to volume in the weighing bottle (100 cc.), and 10 cc. are placed in the Devarda flask, reduced and the ammonia distilled into 100 cc. of the acid. The temperature of the acid is noted and its value in terms of $H_2SO_4$, $KNO_3$ and $NaNO_3$ stated on the container. The acid expands or contracts 0.029 cc. for every degree centigrade above or below the temperature of standardization.

**Oxalic Acid.** — 0.1 N solution. ~6.303 grams of $H_2C_2O_4.SH_2O$ per liter.

*Standardization.* — Titrate 50 cc., measured by a burette, of the solution with 0.1 N NaOH in presence of phenolphthalein indicator. Multiply cc. of caustic used by its factor (titration in presence of phenolphthalein) and divide by 50 to get the factor for the oxalic acid.

Titrate the oxalic acid, hot, with 0.1 N $KMnO_4$ to a faint pink color. Convert cc. of $KMnO_4$ to exact normality and divide by 50 to obtain the factor for the oxalic acid.

**Palladous Chloride.** — Five grams of palladium wire are dissolved in mixture of 30 cc. of hydrochloric and 2 cc. of nitric acid, this evaporated just to dryness on a water bath, redissolved in 5 cc. of hydrochloric acid and 25 cc. of water, and warmed until solution is complete. It is diluted to 750 cc. and contains about 1% of palladous chloride. It will absorb about two-thirds of its volume of hydrogen.

**Paraffin.** — Dissolve in carbon tetrachloride and use solution for reagent labels.

**Peroxide Solution.** — Dissolve 4 grams of sodium peroxide in 125 cc. of dilute sulphuric acid (1 of acid to 3 of water), and dilute to 500 cc. Used in titanium colorimetric determinations.

**Standard Potassium Dichromate.** — The reaction of potassium dichromate with iron may be represented as follows: —

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl = 6FeCl_2 + 2CrCl_3 + 2KCl + 7H_2O$$

When oxygen reacts with ferrous salts, the following reaction takes place:

$$6FeCl_2 + 6HCl + 3O = 6FeCl_3 + 3H_2O.$$

Comparing this reaction with that of dichromate, it is evident that a normal solution of dichromate contains one-sixth of the molecular weight of $K_2Cr_2O_7$ per liter, namely, 49.033 grams. For general use it is convenient to have two strengths of this solution, N/5 for ores high in iron and N/10 for products containing smaller amounts. See Introduction § 25.

*Standardization.* — For N/5 solution 9.807 grams of the recrystallized dehydrated salt are dissolved and made up to one liter; N/10 potassium dichromate contains 4.9033 grams of the pure salt per liter. It is advisable to allow the solution to stand a few hours before standardization. The Sibley iron ore furnished by the U. S. Bureau of Standards, Washington, D. C., is recommended as the ultimate standard. Other ores uniform in iron may be standardized against the Sibley ore and used as standards. The ore in question contains 69.20% of Fe (1914). For accurate work it is desirable to use a chamber burette with graduations from 75 to 90 cc. in tenths and from 90 to 100 in twentieths of a cc. A titration of 90 to 100 cc. of the dichromate would require 0.9 to 1.1 grams of iron for a fifth normal solution and half this amount for a tenth normal solution of dichromate. In the first case 1.4 grams of Sibley iron ore should be taken, for N/10 0.7 gram of the ore. The ore is best dissolved in strong HCl, adding a few drops of stannous chloride solution and heating just below boiling. In case of an ore or iron ore briquette, containing silica in an appreciable amount, a carbonate fusion of the residue may be necessary. Reduction and titration of the ore is done exactly as prescribed in chapter on Iron.

The equivalent iron in the ore divided by the cc. titration required for complete oxidation gives the value in terms of grams per cc., e.g., 1.4 grams of ore containing 69.2% of Fe required a titration of 95 cc. of $K_2Cr_2O_7$ solution, then,

$$1 \text{ cc.} = \frac{(69.2 \times 1.4)}{100} \div 95 = 0.0102 \text{ gram of Fe.}$$

**Optional Methods for Standardization of Potassium Dichromate**

It is not always possible to use the method of standardization with a standard ore, and chamber burettes may not be available. The following methods are reliable.

*First. Optional Method. Standardization against Pure Iron.* — About 0.25 gram of pure iron wire are dissolved in an Erlenmeyer flask with Bunsen valve. Before adding the iron 20 cc. of the dilute sulphuric acid (5N desk reagent) are added and about 2 grams of sodium bicarbonate. This displaces the air with $CO_2$. The wire is dropped in and the rubber stopper carrying the valve inserted. When the reaction has ceased and the iron is in complete solution, the dichromate solution is added until the ferrous iron is just oxidized to ferric state, the end-point being recognized by an outside indicator (1% solution of potassium ferricyanide being placed in drops on a white tile with depressions). Ferrous iron produces a blue color, ferric iron only a yellowish color with the indicator.

*Second. Optional Method.* — 50 cc. of the potassium dichromate solution are pipetted or measured out by a burette into a 300 cc. glass-stoppered bottle. 150 cc. of water are added and 5 cc. of conc. sulphuric acid. After cooling under a tap, 10 cc. of 25% potassium iodide are added, the liberated iodine is now titrated with 0.1 N thiosulphate solution, using starch indicator. The potassium dichromate factor is obtained by multiplying the cc. of thiosulphate by its normality factor and dividing by 50. See Introduction, pages 11, 14.

**Potassium Dichromate.** — Four per cent solution. 40 grams of $K_2Cr_2O_7$ per liter.

**Potassium Chromate.** — Ten per cent solution of neutral potassium chromate.

**Potassium Ferricyanide,** $K_3Fe(CN)_6$. — The salt should be free of ferrocyanide, as this produces a blue color with ferric salts, which would destroy the end-point. It is advisable to wash off the salt before using. A crystal the size of a pinhead dissolved in 50 cc. of water is sufficient for a series of determinations. The solution should be made up fresh for each set of determinations.

**Potassium Ferrocyanide,** *Standard Solution for Zinc Determination.* — 21.55 grams of the crystallized salt per liter. (1 cc. of 0.5 gram sample is equal to about 1%.)

*Standardization.* — Low's Method. — Weigh carefully 0.2 gram of pure zinc, place in an 8 oz. flask and add 10 cc. of conc. hydrochloric acid (sp.gr. 1.2). When the zinc has dissolved, dilute with 25 cc. of water, add a few drops of litmus solution, and make slightly alkaline with ammonia. Again acidify with hydrochloric acid, adding 3 cc. in excess. Dilute to about 250 cc. with hot water, heat to nearly boiling and titrate with the ferrocyanide solution using a 15% uranium nitrate solution as an outside indicator, making the tests as in case of the dichromate titration of iron. A brown tinge obtained by

adding a drop of the titrated solution to a drop of the uranium nitrate on a white tile is the end-point desired. It is advisable to divide the solution titrated, adding the reserve in portions until the entire amount has been titrated. This avoids overrunning the end-point.

**Potassium Ferrocyanide** *for Zinc Determinations.* — 43.1 grams of pure salt in 1000 cc. of water. One cc. = approximately 0.010 Zn. This solution should be allowed to stand about four weeks before using.

*Standardization.* — *New Jersey Zinc Co. Method.* — Weigh into tall 400 cc. beakers several portions of C.P. zinc, using about 0.35 gram. Cover with water and dissolve in 10 cc. of hydrochloric acid (sp.gr. 1.2). Now add 13 cc. of ammonia (sp.gr. 0.9), make acid with hydrochloric acid, and add 3 cc. excess. Add 0.03 or 0.04 milligram of ferrous iron in the form of a ferrous sulphate solution and dilute to about 200 cc. with distilled water. Heat to boiling and titrate as follows: About one-quarter of the solution is reserved in a small beaker and the ferrocyanide added to the main solution with vigorous stirring. The solution takes on a blue color, which changes to a creamy white when an excess of ferrocyanide is added. Now add a few cc. more and pour in the reserved portion of zinc solution, excepting about 5 or 10 cc. Add ferrocyanide until the end-point is reached and add about $\frac{1}{2}$ cc. more. The last of the reserved zinc solution is then poured into the main beaker, washing out the small beaker with a portion of the main solution, and the ferrocyanide added drop by drop until the blue color fades sharply to a pea-green with one drop of ferrocyanide. This is the end-point. Repeat until satisfactory standards are obtained.

**Potassium fluoride** solution; made by dissolving 1000 grams of potassium fluoride in about 1200 cc. of hot, $CO_2$-free water, then neutralizing the solution with hydrofluoric acid or potassium hydroxide as the reagent may require, using 5 cc. of phenolphthalein as indicator. Dilute sulphuric acid may be used in place of hydrofluoric acid in the final acid adjustment to get a neutral product. One cc. of the solution in 10 cc. of $CO_2$-free water should appear a faint pink. The concentrated mix is filtered if necessary and then diluted to 2000 cc. with $CO_2$-free water. The gravity will now be approximately 1.32 or about 35° Bé. One cc. contains 0.5 g. of potassium fluoride.

**Potassium Hydroxide.** — (*a*) For carbon dioxide determination, 500 grams of the commercial hydrate are dissolved in 1 liter of water.

*Absorption Capacity.* — One cc. absorbs 40 cc. of $CO_2$.

(*b*) For the preparation of potassium pyrogallate for special work, 120 grams of the commercial hydrate are dissolved in 100 cc. of water.

**Potassium Iodide Solution.** — Dissolve 250 grams of potassium iodide free from iodate in distilled water and dilute to 1000 cc.

**Potassium Nitrate Standard.** — The purest nitrate that can be obtained is recrystallized in small crystals, by stirring, during the cooling of the supersaturated concentrated solution, and dried first at 100° C. for several hours and then at 210° C. to constant weight. Chlorides, sulphates, carbonates, lime, magnesium and sodium are tested for and if present are determined and allowance made.

Used as a standard in the Devarda method for nitrate determination.

**Potassium Permanganate.** — For oxidation purposes. Two per cent solution filtered free of dioxide through asbestos is required.

**Potassium. Permanganate, Standard Solutions.** — As in case of potassium dichromate, it is convenient to have two standard solutions, N/5 and N/10. (0.2 N and 0.1 N)

Since commercial potassium permanganate is seldom pure, it is necessary to determine its exact value by standardization. This is commonly accomplished by any of the following methods:

(*a*) By a standard electrolytic iron solution.

$$2KMnO_4 + 10Fe + 9H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O + H_2.$$

(*b*) By ferrous salt solution, e.g., $(NH_4)_2SO_4.FeSO_4.6H_2O$.

(*c*) By oxalic acid or an oxalate.

**Reaction.** — $$2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 10CO_2 + 8H_2O.$$

From the reactions above it is evident that $2KMnO_4$ will oxidize 10Fe or $5Na_2C_2O_4$. $2KMnO_4 = K_2O + 2MnO + 5O$, hence a normal solution would contain one-fifth of the molecular weight of $KMnO_4$ = 31.6 grams of the pure salt. Hence a N/5 solution would contain 6.32 grams per liter and a N/10 solution 3.16 grams.

Standard 0.1 N potassium permanganate contains 3.161 grams of $KMnO_4$ per liter and the 0.2 N (or N/5) contains twice this amount.

It is advisable to dissolve 6.4 grams of the salt in about 500 cc. of hot water and filter the solution through asbestos to remove any dioxide of manganese that may be present, as $MnO_2$ aids in the decomposition of $KMnO_4$ solution. The reagent should be kept tightly sealed in a dark bottle well protected from the light. This solution should stand two or three days before standardization. The solution is diluted to 1000 cc. for a 0.2 N solution or to 2000 cc. for a 0.1 N solution.

*Standardization.* (*a*) *Iron Wire in Sulphate Solution.* — Standard iron wire, as furnished by chemical supply houses, with the percentage of iron given (usually about 99.8% of Fe) gives results, when properly treated, which are practically identical with those obtained by the use of sodium oxalate.

Samples of 0.2000 gm. are weighed out and the weights multiplied by the factor for iron, giving the true weight of iron. 50 cc.

of 20% sulphuric acid are placed in a 250 cc. Erlenmeyer flask, which is fitted with a rubber stopper carrying a Bunsen valve. Into the acid is dropped from one to two grams of sodium bicarbonate in order that the air may be replaced by carbon dioxide and then the sample of wire is introduced and the flask stoppered by the Bunsen valve. The whole is then boiled gently until the iron is completely dissolved, and the boiling continued for a minute or two more. The solution is now cooled, and, after dilution to 150 cc., titrated to the first permanent pink.

$$\frac{\text{Net weight of iron}}{\text{cc. used}} = \text{iron standard.}$$

The atmosphere of $CO_2$ and the Bunsen valve are employed so that oxygen may be kept out of contact with the hot solution. Under these conditions the iron goes into solution completely as $FeSO_4$. The boiling after complete solution is necessary in order that all traces of hydrocarbons from the carbon present in the iron may be expelled. Hydrocarbons reduce permanganate.

The complete reaction is:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

(*b*) *Standardization of $KMnO_4$ against sodium oxalate* is recommended as the most accurate procedure. The salt has no water of crystallization and is not hygroscopic. It can be obtained from the Bureau of Standards with a guarantee of purity. Traces of moisture can be expelled by heating the salt to 120° C. for two hours, then cooling in a desiccator.

The chemistry of the process is as follows:

$$2KMnO_4 \rightarrow K_2O + 2MnO + 5O,$$

$$Na_2C_2O_4 + H_2SO_4 \rightarrow H_2C_2O_4 + Na_2SO_4$$

$$H_2C_2O_4 + O \rightarrow H_2O + 2CO_2$$

$$\text{and so } 5O + 5H_2C_2O_4 \rightarrow 5H_2O + 10CO_2.$$

From these expressions it is seen that

$2KMnO_4 \eqsim 5O \eqsim 5H_2C_2O_4 \eqsim 5Na_2C_2O_4$, and the complete reaction is

$2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$. Since $2KMnO_4 \eqsim 10Fe$, from the reaction $2FeO + O \rightarrow Fe_2O_3$,

$$2Na_2C_2O_4 \eqsim 10Fe.$$

Samples of sodium oxalate of 0.2000 gm. each are weighed and placed in 400 cc. beakers. 200 cc. of water and about 2 cc. of concentrated sulphuric acid are added, and the whole heated to about 70° C. The hot solution is then titrated with permanganate to the first pink color that lasts about a minute. The reaction between permanganate and oxalic acid is slow in starting, but rapid afterward. Care should be taken that the titration be so slow that the solution is not colored throughout by an excess of permanganate until the end. See Introduction § 24.

**Potassium Permanganate.**[1] **Preparation of N/100 Solution.** — Dissolve 0.40 g. of pure potassium permanganate crystals in one liter of redistilled water in a thoroughly clean Florence flask which has been rinsed with the same water. Digest at or near the boiling point for 36 hours. A funnel covered with a watch-glass may be used as a reflux condenser. Cool and allow to stand over night. Without disturbing the sediment of manganese oxides, filter with gentle suction through a 3 in. Büchner funnel lined with ignited asbestos. Both funnel and filter flask should be rinsed with redistilled water. Transfer the permanganate solution to a glass-stoppered bottle free from traces of organic matter. The solution should be kept in the dark when not in use. If the asbestos becomes clogged with oxides these may be dissolved out with hot concentrated hydrochloric acid, followed by washing with redistilled water without disturbance of the pad.

After standing two or three days this permanganate solution may be conveniently standardized against N/50 oxalic acid (0.1261 g. of pure crystals to 100 cc.) or sodium oxalate of similar strength. To 10 cc. of the oxalic acid solution add 10 cc. of 10 per cent sulphuric acid which has been treated with just sufficient permanganate solution to give it a faint pink color. Place in a water bath at 65° C. for a few minutes. Then titrate at once to a definite pink color which persists for at least a minute. Correct for the blank obtained by titrating 10 cc. of the sulphuric acid and the same volume of water to the same end-point. On account of the sensitivity of this reagent it is desirable to check it up rather frequently.

**Potassium or Ammonium Thiocyanate** (*Sulphocyanate*) 0.1 *N Solution.* — About 8 grams of ammonium or 10 grams of potassium salt are dissolved in water and diluted to one liter. The solution is adjusted by titration against the N/10 silver nitrate solution. It is advisable to have 1 cc. of the thiocyanate equivalent to 1 cc. of the silver nitrate solution. Owing to the deliquescence of the thiocyanates the exact amount for a N/10 solution cannot be weighed.

**Potassium Pyrogallate.** — Except for use with the Orsat or Hempel apparatus, this solution should be prepared only when wanted. The most convenient method is to weigh out 5 grams of the solid acid

[1] *Jour. of Ind. and Eng. Ch.*, Feb. 1918.

upon a paper, pour it into a funnel inserted in the reagent bottle, and pour upon it 100 cc. of potassium hydrate. The acid dissolves at once, and the solution is ready for use.

Attention is called to the fact that the use of potassium hydroxide purified by alcohol has given rise to erroneous results.

*Absorption capacity.* — One cc. absorbs 2 cc. of O.

**Salt Solution Standard.** — 16.48 grams of fused C.P. sodium chloride are dissolved in 1 liter of distilled water. 100 cc. of this solution diluted to 1 liter gives a standard solution, each cc. of which contains .001 gram of chlorine.

**Silver Nitrate Standard Solution.** — 4.8 grams of dried silver nitrate crystals are dissolved in one liter of distilled water. Each cc. of this solution is equivalent to approximately .001 gram of chlorine, standardized against the Standard Salt Solution.

Note. N/50 solutions of both sodium chloride and silver nitrate can be used where it is inconvenient to make too many standard solutions, using the proper factors.

**Silver Nitrate** $N/10$. — This solution contains 10.788 grams of Ag or 16.989 grams of $AgNO_3$ per liter. The silver nitrate salt, dried at 120° C., or pure metallic silver may be taken, the required weight of the latter being dissolved in nitric acid and made to volume, or 17.1 grams of the salt dissolved in distilled water and made to 1000 cc. The solution is adjusted to exact decinormal strength by standardizing against a N/10 sodium chloride solution, containing 5.846 grams of pure NaCl per liter.

**Silver, Pure, Preparation of.** — The volumetric methods used for the determination of high percentages of silver employ solutions which should be standardized by metal of the highest purity. For the preparation of this metal, the electrolytic method as described below is preferred by laboratories which are suitably equipped.

By Knorr's method, a solution of silver nitrate from which excess of nitric acid has been removed by evaporation is freed of metallic impurities by adding enough sodium carbonate to precipitate one-tenth of the silver, boiling and filtering. The silver in the filtrate is precipitated by sodium carbonate and the precipitate decomposed without addition of reducing agent, by melting in a crucible. Excess sodium carbonate carried down with the precipitate of silver carbonate will cover the fusion and such as adheres tightly to the metal is readily removed by hydrochloric acid. The metal should be smelted under charcoal.

*For standardizing the decimal solution,* 1 *gram of standard silver is* dissolved in a funnel-closed liter flask by 20 cc. of equal volumes of nitric acid and water. After boiling to decompose nitrous acid the solution is made up to mark with water at room temperature.

When using the standard thiocyanate solution with the object of obtaining very accurate results, it is good practice, instead of using

a standard solution of silver to obtain the standard by titrating, simultaneously with the assays, solutions of known quantities of standard silver approximately equal in amount and dissolved in the same manner as the assays. Volhard's Method for Silver.

**Sodium Bismuthate.** — Prepare as follows: Heat 20 parts of caustic soda nearly to redness in an iron or nickel crucible, and add, in small quantities at a time, 10 parts of basic bismuth nitrate, previously dried in a water oven. Then add 2 parts of sodium peroxide and pour the brownish-yellow fused mass on an iron plate to cool; when cold, break it up in a mortar, extract with water, and collect on an asbestos filter. The residue, after being washed four or five times by decantation, is dried in the water oven, then broken up and passed through a fine sieve.

**Sodium Carbonate.** — 10% solution. 100 grams of $Na_2CO_2$ per liter.

**Sodium Hydroxide.** — Desk reagent. See the beginning of this chapter.

**Sodium Hydroxide.** — Normal solution. 1 cc. of the reagent is equivalent to 0.04904 g. of $H_2SO_4$. Use rubber stoppers for bottles with sodium compounds.

**Preparation of Standard Solution.** — Make up a stock concentrated solution of sodium hydroxide by dissolving sodium hydroxide in water in the proportion of 200 grams of NaOH to 200 cc. of water. Allow this solution to cool and settle in a stoppered bottle for several days. Decant the clear liquid from the precipitate of sodium carbonate into another clean bottle. Add clear barium hydroxide solution until no further precipitate forms. Again allow to settle until clear. Draw off about 175 cc. and dilute to 10 liters with freshly boiled distilled water. Preserve in a stock bottle with a large guard tube filled with soda lime. Determine the exact strength by titrating against pure benzoic acid ($C_6H_5COOH$) or against standard sulphuric acid, using phenolphthalein as indicator. This solution will be approximately one-fourth normal, but do not attempt to adjust it to any exact value. Determine its exact strength and make proper corrections in using it. See chapter on Alkalimetry and Acidimetry.

This should be made of such strength that 1 cc. is equal to 1 cc. of the standard acid, 2 cc. of methyl red being used as indicator. Ten cc. of the acid are diluted to 500 cc. and the alkali added until the color of the indicator changes from a red to a straw color.

*Sodium Hydroxide. — Tenth Normal Solution.* — For determination of phosphorus by the alkali volumetric method, consult chapter on Phosphorus.

**Sodium Hydroxide Solution, Alcoholic.** — Dissolve pure sodium hydroxide in 95 per cent alcohol in the proportion of about 22 grams per 1000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used; it will keep colorless

longer if the alcohol is previously treated with NaOH (about 80 g. to 1000 cc.), kept at about 50° C. for 15 days, and then distilled.

*N/5 Sodium Oxalate.* — $Na_2C_2O_4$ reacts with $KMnO_4$ as follows:

$$5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 10CO_2 + 8H_2O.$$

Hence $5Na_2C_2O_4$ divided by 10 or 134 divided by 2 = 67 grams per liter = a normal sodium oxalate solution. A N/5 solution requires 13.4 grams $Na_2C_2O_4$ per liter.

**Sodium Sulphide.** — Ten per cent solution, made from colorless crystals. Sodium sulphide may be made by saturating a strong solution of sodium hydroxide with hydrogen sulphide gas, and then adding an equal volume of the sodium hydroxide. The solution is diluted to required volume, allowed to stand several days, and filtered.

**Sodium metabisulphite.** — Solid salt of $Na_2S_2O_5$.

**Sodium Thiosulphate.** — Used in copper determinations. 7.5 grams of the salt, $Na_2S_2O_3.5H_2O$, are dissolved and made to 2 liters with water. The solution is standardized against a copper solution containing 1 gram of pure copper per liter. 1 cc. = 0.001 gram of Cu. Approximately the same amount of copper in the same volume of solution, is taken as is to be determined by the assay. For high-grade copper ores and crude copper, etc., it is advisable to prepare a standard thiosulphate solution ten times the above strength. The copper solution is made slightly ammoniacal and then acid with acetic acid. Potassium or sodium iodide crystals, free from iodate, are added and the liberated iodine titrated with the standard thiosulphate. (See Procedure under Copper.)

**Sodium Thiosulphate, Standard 0.1 N Solution for General Analysis**

Consult Introduction § 18–27. Sodium thiosulphate reacts with iodine as follows:

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_2O_6.$$

1 gram molecule of thiosulphate is equivalent to 1 atom of iodine = 1 atom of hydrogen, hence a tenth normal solution is equal to one-tenth the molecular weight of the salt per liter, e.g., 24.822 grams of $Na_2S_2O_3.5H_2O$; generally a slight excess is taken — 25 grams of the crystallized salt. It is advisable to make up 5 to 10 liters of the solution, taking 125 to 250 grams of sodium thiosulphate crystals and making up to volume with distilled water, boiled free of carbon dioxide. The solution is allowed to stand a week to ten days, and then standardized against pure, resublimed iodine.

*Standardization.* — About 0.5 gram of the purified iodine is placed in a weighing bottle containing a known amount of saturated potassium iodide solution (2 to 3 grams of KI free from $KIO_3$ dissolved

in about ½ cc. of $H_2O$), the increased weight of the bottle, due to the iodine, being noted. The bottle and iodine are placed in a beaker containing about 200 cc. of 1% potassium iodide solution (1 gram KI per 200 cc.), the stopper removed with a glass fork and the iodide titrated with the thiosulphate to be standardized.

**Calculation.** — The weight of the iodine taken, divided by the cc. of thiosulphate required, gives the value of 1 cc. of the reagent; this result divided by 0.012692 gives the normality factor.

NOTE. The thiosulphate solution may be standardized against iodine, which has been liberated from potassium iodide in presence of hydrochloric acid by a known amount of standard potassium bi-iodate, a salt which may be obtained exceedingly pure.

$$KIO_3.HIO_3 + 10KI + 11HCl = 11KCl + 6H_2O + 6I_2.$$

A tenth normal solution contains 3.2496 grams of the pure salt per liter. (One cc. of this will liberate 0.012692 gram of iodine from potassium iodide.) The purity of the salt should be established by standardizing against thiosulphate, which has been freshly tested against pure resublimed iodine.

About 5 grams of potassium iodide (free from iodate) are dissolved in the least amount of water that is necessary to effect solution, and 10 cc. of dilute hydrochloric acid (1:2) are added, and then 50 cc. of the standard bi-iodate solution. The solution is diluted to about 250 cc. and the liberated iodine titrated with the thiosulphate reagent; 50 cc. will be required if the reagents are exactly tenth normal.

**Optional Methods of Standardization.** — The thiosulphate may be standardized against standard 0.1 N potassium dichromate (4.9033 grams of pure $K_2Cr_2O_7$ per liter of solution) as follows. Place in a beaker 100 cc. of distilled water and 10 cc. of a 25% solution of potassium iodide. Now add from a burette 50 cc. of the standard N/10 potassium dichromate and 10 cc. of conc. HCl, and titrate the liberated iodine with standard N/10 thiosulphate reagent. When the yellow color has almost disappeared, add about 2 cc. of starch solution and continue the titration until the blue changes to a sea-green. The cc. of dichromate taken divided by the cc. of thiosulphate required will give the factor in terms of tenth normal solution.

Tenth normal potassium permanganate may be used to liberate the iodine in place of the dichromate, if desired, and the thiosulphate titration made as usual.

It is best to leave the thiosulphate solution as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal strength. Preserve in a stock bottle provided with a guard tube filled with soda lime.

**Sodium Thiosulphate Solution.** — N/100 solution is made as needed from the N/10 stock solution.

**Sulphuric Acid.** — Desk reagents. See first part of this chapter.

**Sulphuric Acid.** — Standard. See chapter on Acidimetry and Alkalimetry.

**Sulphuric Acid Solution, Half Normal.** - Add about 15 cc. of sulphuric acid (1.84 specific gravity) to distilled water, cool and dilute to 1000 cc. Determine the exact strength by titrating against freshly standardized sodium hydroxide or by any other accurate method. Either adjust to exactly half normal strength or leave as originally made, applying appropriate correction. See Introduction, § 7, to make up an approximate strength without the use of balances.

**Stannous Chloride Solution.** — The reagent is prepared by dissolving 2 grams of stannous chloride crystals in hot concentrated hydrochloric acid and making up to 1 liter. The solution should be kept in a dark bottle to which the titrating burette is attached in such a way that the liquid may be siphoned out into this, as shown in the illustration, Fig. 83. The air entering the bottle passes through phosphorous or pyrogallic acid to remove the oxygen. In this way, protected from the air, the reagent will keep nearly constant for several weeks. It is advisable, however, to restandardize the solution about every ten to fifteen days. One cc. will be equivalent to about 0.001 gram of Fe.

**Stannous Chloride, Strong.** — Sixty grams of the crystallized salt are dissolved in 600 cc. of strong HCl and made up to one liter. The solution should be kept well stoppered.

**Starch Solution.** — Five grams of potato or arrowroot starch are rubbed to a paste in cold water, 200 cc. of hot water stirred in, the starch dissolved by boiling, and then poured into about two liters of hot water and boiled for a few minutes.

*Preservatives.* — Various preservatives are used for preserving the starch solution. A few cc. of 5% NaOH solution added to the boiling solution above will preserve the starch.

*Salicylic acid,* 10 cc. of 1% solution per liter is a good preservative.

*Chloroform,* a few drops per liter of starch solution.

*Zinc chloride solution,* a few cc. of 10% solution per liter.

*Sodium chloride and acetic acid.* The starch solution is prepared by adding to 500 cc. of a saturated sodium chloride solution (filtered) 100 cc. of 80% acetic acid and 3 grams of starch, mixing cold. The solution is now brought to boiling and boiled about two minutes. The solution thus prepared keeps indefinitely.

**Tartrate Solution, Alkaline.** — Twenty-five grams of C.P. sodium potassium tartrate, $NaKC_4H_4O_6.4H_2O$, is dissolved in 50 cc. of water. A little ammonia is added and then sodium sulphide solution. After settling some time the reagent is filtered. The filtrate is acidified with hydrochloric acid, boiled free of $H_2S$ and again made ammoniacal and diluted to 100 cc.

**Thymol Solution** 1%. — The thymol is dissolved in a little glacial acetic acid containing 10% of ethyl alcohol, and this solution added to concentrated sulphuric acid. Addition of the thymol directly to the

acid would produce a colored solution. The reagent should be kept protected from strong light, otherwise it will become colored.

**Zinc, Amalgamated.** — This is best prepared by dissolving 5 grams of mercury in 25 cc. of concentrated nitric acid with an equal volume of water, 250 cc. of water are added and the solution poured into 500 grams of shot zinc, 20-mesh. When thoroughly amalgamated the solution is poured off, and the zinc dried.

## PREPARATION AND USES OF CHEMICAL INDICATORS[1]

**Litmus.** — Red with acids, blue with alkalies.

*Preparation.* — A solution obtained by extracting the crushed cubes with hot water may be used after allowing the insoluble matter to settle out. With such a solution the color change is not sharp. The best method of preparation is as follows: The unbroken cubes are digested for some time with several portions of warm (85%) alcohol. The alcoholic solution contains undesirable compounds and is thrown away. The residue is boiled with water, allowed to stand several days and the solution siphoned off. This blue solution is made slightly acid with acetic acid, evaporated to a syrup, and then mixed with a large amount of 95% alcohol. By this means the desired coloring matter (azolitmin) is precipitated. It is filtered off, washed with hot alcohol and dissolved in sufficient hot water to give a solution 3 or 4 drops of which will impart a distinct blue color to 50 cc. of water. Tincture of litmus should be preserved in a wide-mouthed bottle loosely stoppered with a plug of cotton so as to exclude dust while permitting the access of air. Litmus gives good results with mineral acids, oxalic acid and caustic alkalies; if used in titrating carbonates the solution must be boiled to expel $CO_2$ as it affects the indicator.

**Methyl Orange.** — Pink with acids, yellow with alkalies.

*Preparation.* — One gram is dissolved in a liter of hot water. If not clear after cooling, it should be filtered. Methyl orange is not very sensitive to acids. For this reason it should not be used with organic acids. Because of its low sensitiveness to acids it may be used for the titration of carbonates in cold solution. It gives good results with ammonia.

**Phenolphthalein.** — Colorless with acids, red with alkalies.

*Preparation.* — One gram is dissolved in a liter of about 85% alcohol. Phenolphthalein is very sensitive to acids, less sensitive to alkalies. Can be used with mineral acids and with most organic acids. Carbonates give indistinct end-points unless solution is boiled to expel $CO_2$. Useless with ammonia.

**Rosolic Acid.** — Yellow with acids, violet red with alkalies.

*Preparation.* — Dissolve 2 grams in a liter of 85% alcohol. Rosolic acid can be used with mineral acids including sulphurous acid and with oxalic acid, but not with other organic acids. In neutralizing sulphurous acid with ammonia this indicator changes when the normal sulphite is formed. It is somewhat affected by carbonic acid.

**Cochineal.** — Yellowish red with acids, violet with alkalies. Cannot be used in presence of iron, alumina, or acetates. Cochineal may be used for the titration of ammonia and for alkali carbonates and bicarbonates in cold solution. Carminic acid is the essential compound in this indicator and is preferable to the indicator made from cochineal.

[1] By H. J. Laverty, *Lefax Staff.*

*Preparation.* — One part of the crushed insect is extracted with 10 parts of 25% alcohol. The extract when filtered is ready for use.

**Phenacetolin.** — Color with mineral acids is golden yellow. Color with alkali carbonates and ammonia is pink.

*Preparation.* — Dissolve 2 grams in a liter of 50% alcohol.

**Lacmoid.** — Red with acids, blue with alkalies.

*Preparation.* — Dissolve in dilute alcohol, 3 grams per liter.

**Turmeric Paper.** — Yellow with acids, brown with alkalies.

*Preparation.* — Pieces of the root are first digested with several portions of water to remove undesired matter, and then with alcohol. Paper is moistened with the alcoholic solution and dried in the dark. It is used in titrating highly colored solutions where an inside indicator cannot be used, and for the detection of borates. When moistened with a solution containing free boric acid and then dried, a brown color results which is not destroyed by dilute sulphuric or hydrochloric acids and is changed by alkali hydroxide to a bluish-black color.

## STANDARD LABORATORY APPARATUS [1]

### VOLUMETRIC APPARATUS

Very great advances have been made in the United States toward the standardization of volumetric apparatus, first by the U. S. Bureau of Standards and more recently by a committee representing manufacturing chemists. The latter, in coöperation with the manufacturers and dealers of chemical apparatus, has completed its recommendations for the standardization of several types of volumetric glassware, in regard to types, quality, design, workmanship and units of capacity. This is a commendable advance but while it will insure a supply of standard volumetric glassware, if the movement is generally supported by both makers and users, it does not preclude the necessity of recalibration or verification by the chemist himself. This is especially evident when we recall the fact that volumetric chemical analyses are often reliably calculated to 0.01%, whereas the volumetric glassware may be in error to such an extent as to make the 0.10% figure unreliable.

The following principles, procedures and tables for testing and calibrating volumetric apparatus, except for a few additions, were obtained from publications of the U. S. Bureau of Standards.

**Preparation of Apparatus.** — Having selected standard apparatus it should be thoroughly prepared for calibration by removing all foreign material, dirt, grease, etc., from the surface by one of the following methods:

1. By immersion for several hours in a concentrated solution of caustic soda in 95% alcohol, after which it should be washed with sulphuric acid and water and allowed to drain until dry.

2. By immersion in fuming sulphuric acid for a few minutes, washing with water, then with caustic soda solution and finally with water and allowing to drain until dry.

3. Concentrated sulphuric acid saturated with chromic acid is a very efficient cleaning solution. This may be substituted for the fuming sulphuric acid in the above procedure.

4. Another method by which small apparatus, such as flasks, burettes, pipettes, etc., may be quickly and thoroughly cleaned but with which great precaution should be exercised is as follows: — To two volumes (10–20 cc.) of 95% alcohol in the apparatus, add one volume (5–10 cc.) of concentrated nitric acid. This mixture develops a rather violent action in from one to five minutes, generates much

[1] Contributed by R. M. Meiklejohn and J. S. Coye.

heat and thoroughly cleans the surface with which it comes in contact. This mixture should be used very cautiously and sparingly and should not be confined. The action is accelerated by warming and is almost explosive at times. The change in volume of the apparatus and thermal hysteresis due to the heating by this method

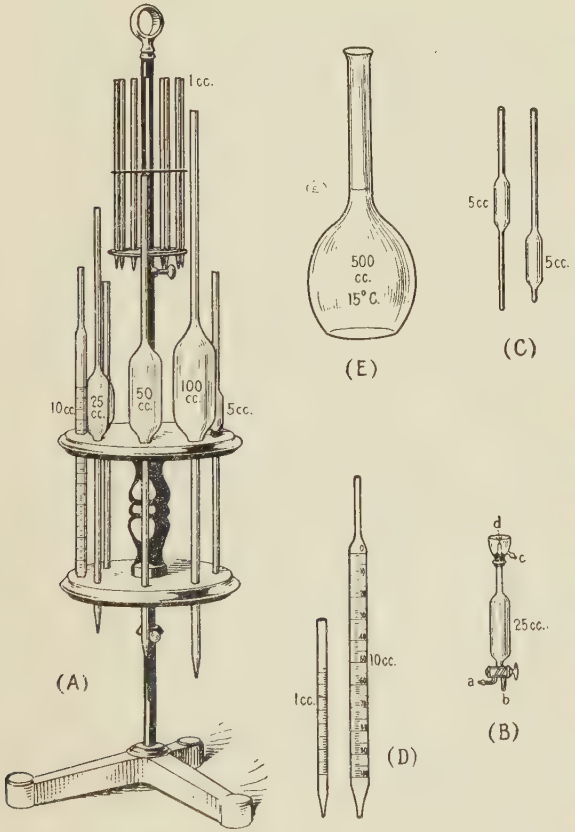



FIG. 148. Volumetric Measuring Apparatus.

of cleaning can usually be neglected if a sufficient drainage and cooling period is employed.

**Stop-cock Grease.** — Soft grease. Thoroughly mix, by melting and stirring, three parts of vaseline and one part of beeswax.

Hard grease. Add one part (i.e. 1 : 4) of soft black rubber in small bits to the above mixture, heat to 140–150° C., and stir constantly until thoroughly incorporated.

**Measurement of Capacity.** — There are two general methods in use by which the capacity of an apparatus is determined, the choice being determined by the character of the apparatus; namely, direct measurement and calculation of capacity from the weight of water which it contains or delivers.

**Direct Measurement.** — This method is especially applicable to the testing or calibration of flasks and consists in allowing water at a constant temperature to flow from a standard pipette, which is graduated at the lower end, into the flask at a rate of flow standard for the pipette until the flask is filled to its graduation mark. The volume (capacity) of the flask is then read off on the graduation of the standard pipette, making any instrumental correction applying to the standard pipette as determined by the procedure of calculation of capacity at 20° C. from the weight of water delivered under the standard conditions of outflow. It is evident that this method gives a direct measurement of capacity at the standard temperature of 20° C. regardless of the temperature of water except that the water should be maintained at a constant temperature throughout the entire operation. This change of temperature is the only inherent error in the procedure, except the error of unequal expansion of the two glasses, which is assumed to be negligible. The chief disadvantage in the procedure is that a separate standard pipette is necessary for each size of flask, and consequently is only applicable when a large number of flasks are to be calibrated.

**Calculation from Weight of Water.** — The quantity sought in this case is the actual volume of water contained or delivered by the apparatus at the standard temperature of 20° C. and is calculated from quantities observed, obtained from tables, and calculated.

Quantities observed.

V = nominal capacity of apparatus (milliliters).
t = temperature of water weighed.
a = apparent weight in air of water.
b = buoyancy constant (Table 1).

Quantities obtained from Tables.

$d_t$ = density of water at t° C. (Table 2).
M = mass of water having a volume V at t° C. (Table 2 $d_t \times V$).
A = apparent weight in air of water having volume V at t° C. (Table 3).

Quantities calculated.

v = volume of water at t° C. (milliliters).
C = capacity of instrument at standard temperature 20° C.

The capacity v at the observed temperature t° C. is first calculated. This may be accomplished by one of three formulæ according to the precision desired.

In all cases where the greatest precision is desired the following formula is used.

1. $$v = \frac{a}{d_t - b}$$

$d_t$ is obtained from a table of water densities.

b may be obtained from tables or may be observed directly as follows: — Place a hollow sealed glass bulb of known volume (about 1000 ml.) and mass on one pan of a balance and an equal mass of brass weights on the other pan of the balance. The additional weight w required on the bulb pan for a balance is then the buoyancy of the volume v of the bulb for the atmospheric conditions prevailing, or $b = \frac{w}{v}$ = grams per milliliter. The mass of the bulb is its true weight in vacuum and may be calculated from its apparent weight by adding, to its apparent weight in air, the weight of an equivalent volume of air at the temperature and atmospheric conditions prevailing at the time the apparent weight was obtained minus the weight of a volume of air equal to the volume of brass weights used in obtaining the weight in air.

*Example:*

Volume displaced by the bulb = 950 ml. = .950 liter = $V_b$.

Apparent weight of bulb at 22° C. and 740 mm. mercury (corrected to 0° C. and standard gravity) with brass weights = 218.124 gms.

Then $\frac{218.124}{8.4}$ = 25.95 ml. = .02595 liter = $V_w$ or volume of brass weights.

Then $$218.124 + \frac{(V_b - V_w) \times 1.2930}{1 + .00367 \times t} \times \frac{P}{760} = \text{true weight of bulb.}$$

Or $$218.124 + \frac{(.950 - .02595) \times 1.2930}{1 + .00367 \times 22} \times \frac{740}{760} = 219.2005.$$

This true weight or mass of the bulb is then the value to be used in determining the buoyancy constant for the particular atmospheric conditions prevailing or

$$\text{buoyancy constant} = \frac{219.2005 - 218.124}{950.} = .001133 \text{ gms.}$$

or 1.133 mgs. per milliliter.

This figure is obtained by assuming the air to be dry and free from carbon dioxide. The value of 1.2930 gms. as the weight of one liter of air at 0° C. and 760 mm. pressure at sea level is obtained only under these conditions and consequently requires corrections for the carbon dioxide and moisture content of the air at the time the weight is taken. For ordinary work Table 1, as prepared by the

U. S. Bureau of Standards, gives the buoyancy constant of sufficient accuracy.

When V is a round number, the following approximate formula simplifies the calculation.

2. $v = V + a + (V \times b) - M.$

M = the mass of water having a volume V at t° C. and may be calculated from water density tables. (Table 2 $d_t \times V$.)

b is obtained as above.

If v – V is less than 1/1000 v, the error will not be greater than 1/200000 v.

When V is a round number and the buoyancy constant is not observed, the following formula may be applied.

3. $v = V + a - A.$

A may be obtained from tables. (Table 3.) The values obtained by this formula are equal in accuracy to those obtained by formula 2.

After calculating v by one of the above formulæ, the capacity C of the apparatus at 20° C. is calculated by the formula

$$C = v + .000025\ v\ (20 - t).$$

The value .000025 is taken as the average cubical expansion of glass.

Values for .000025 v (20 – t) have been calculated and tabulated by the U. S. Bureau of Standards.

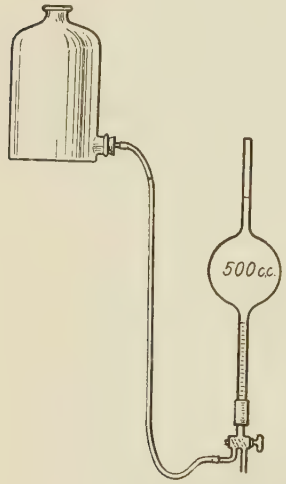



Fig. 149. Morse-Blalock Apparatus in Position for Calibrating Flasks.

**Flasks.** — Flasks are most readily tested or calibrated by direct measurement from a standard pipette as previously described. When the weighing method is employed, the procedure is as follows: — The flask is suspended from the left arm of the balance, thus leaving space for weights on the balance pan. A weight somewhat greater than the total weight of the flask when filled to the mark with water is placed on the right balance pan. The clean dry empty flask with stopper is then balanced by placing the necessary weights on the pan carrying the flask. The flask is next filled to the mark with water at a definite constant temperature t° C. and again balanced by removing weights. The weights removed give the apparent weight (a) in air of the water at temperature t° C. and p barometric pressure (uncorrected). The capacity C at 20° C. of the flask of nominal volume V is then calculated as previously described.

*Example:* (500 ml. flask).

519.710
20.950
a = 498.760 apparent weight in air of water at 17° C. and 735 mm.
$d_t$ = .9988 density of water at 17° C. (gms. per milliliter).
b = .001037 buoyancy constant. (See Table 1.)

Then

$$v = \frac{a}{d_t - b} = \frac{498.760}{9988 - .0010} = 499.88 \text{ ml. at } 17^\circ \text{ C.}$$

and

$$C = v + .000025\, v\, (20 - t) - 499.88 + (.000025 \times 499.88 \times 3) = 499.02 \text{ ml. at } 20^\circ \text{ C.}$$

Another procedure of calculating the capacity of a flask from the weight in air of the water contained or delivered which eliminates any error in weighing due to condensation of moisture on the flask is as follows:

A flask of similar type and equal volume is used as the counterpoise on the opposite balance arm when obtaining the weight "a" of water at the temperature of the air.

Then

$$v = \frac{a}{d_t - b} = \text{capacity in ml. at } t^\circ \text{ C.}$$

and

$$C = v + .000025\, V\, (20 - t) = \text{ml. at } 20^\circ \text{ C.}$$

The water used for this work should be pure and freed from dissolved air by previous boiling and should not be allowed to wet the flask above the graduation mark. When filling the flask it should be shaken occasionally to insure complete wetting and removal of any dust, etc., from the glass surface, which might cause the occlusion of minute air bubbles. When possible these dust particles should be floated off from the top of the water before making up to the graduation mark. If the graduation mark is found to be in error, it may be corrected by making a preliminary mark and subsequently verifying by the above procedure.

**Pipette.** — Pipettes are most conveniently tested and calibrated by filling once with water at constant temperature t° C. and emptying, then filling again to the mark and emptying into a tared flask. By weighing the flask the apparent weight of water at t° C. delivered is obtained. The capacity of the pipette at 20° C. is then calculated as previously described.

*Example:*

Standardization of Pipette B–902
a = 49.8283 = wt. of water delivered at 24.1° C. and 740 mm. pressure.
From Tables 1 and 2:
b = .00101 gms.
$d_t$ = .99732

then

$$V = \frac{a}{d_t - b} = \frac{49.8283}{.99631} = 50.0128 \text{ ml. at } 24.1^\circ \text{ C.}$$

and

$$C = v + .000025 \times V \times (20 - t) = 50.0128 - .005 = 50.008 \text{ ml. at } 20^\circ \text{ C.}$$

The method of draining the pipette should be the same when calibrating as when being used. The most generally accepted method of draining a pipette is to allow it to run out freely until emptied, then the tip is touched against the wetted wall of the vessel into which delivery is being made. The shape and character of the tip and

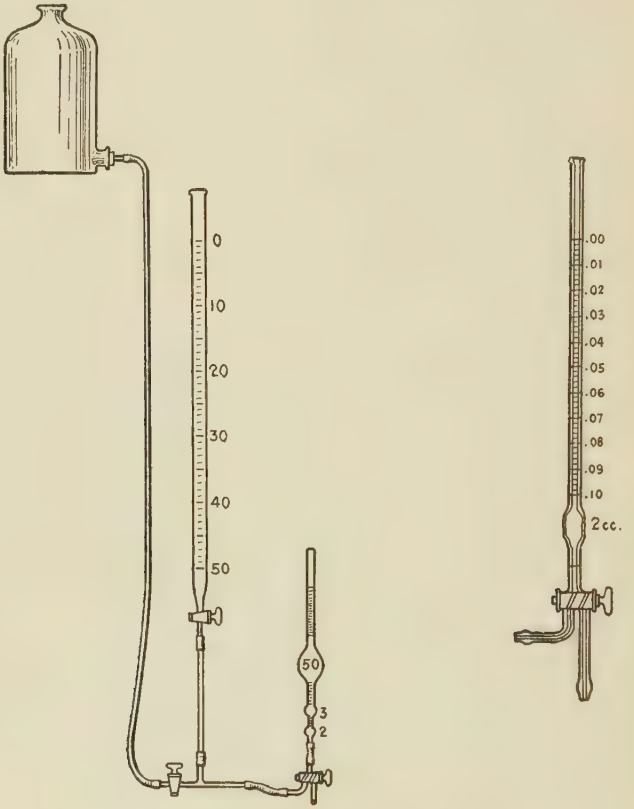



FIG. 150. Volumetric Calibrating Apparatus.

size of the meniscus stem should be as specified by the U. S. Bureau of Standards [1] and the committee representing the Manufacturing Chemists.[2]

A pipette may also be calibrated by connecting up with a standard pipette as shown in Fig. 150. The water from the standard is al-

[1] Committee on Apparatus Standardization of the Manufacturing Chemists' Association of the U. S.

[2] Scientific Papers No. 92 and Circular No. 19.

lowed to flow by gravity into the pipette being tested, the standardization being conducted at 20° C.

**Burettes.** — Type, design, size, etc., of burettes have been standardized by the U. S. Bureau of Standards and the committee representing the chemical manufacturers to such an extent as to make the calibration of them simple and reliable. These specifications are such as to give the proper rate of out-flow to make the residue and after-flow negligible when calibrated under conditions of out-flow indicated for each particular type of burette.

In calibrating a burette, the weight of water at constant temperature and pressure which is delivered under standard conditions of out-flow is determined for each graduation of the burette as desired, always beginning at the zero graduation each time. The volume of water for each increment is then calculated as previously described. It is very important that the burette types which have been specified by the standardization committee be selected for calibration.

*Example:*

Standardization of Burette 1394.

Each increment is weighed and the weight, temperature and pressure recorded, $d_t$ and b obtained from Tables 1 and 2 and the formula $v = \frac{a}{d_t - b}$ and $C = vt\ .000025 \times V \times (20 - t)$ applied to each increment. The results may be tabulated as follows:

| *Point* | *a* | *C.* | *Error* |
|---|---|---|---|
| 5 ml. | 4.9562 | 4.98 | − .02 |
| 10 " | 9.9463 | 9.99 | − 01 |
| 15 " | 14.9220 | 14.98 | − .02 |
| 20 " | 19.9158 | 20.00 | − .00 |
| 25 " | 24.9019 | 25.00 | − .00 |
| 30 " | 29.8572 | 29.98 | − .02 |
| 35 " | 34.8254 | 34.96 | − .04 |
| 40 " | 39.8001 | 39.96 | − .04 |
| 45 " | 44.8419 | 45.02 | + .02 |
| 50 " | 49.7809 | 49.99 | − .01 |

A burette may be standardized against a second standard burette or pipette by filling the one to be tested with water (20° C.) and after connecting to the standard allowing the water to flow into the standard. The connections should be filled with water (free from air bubbles) and the water should stand at the 0 point in the measuring apparatus. See Fig. 150. The upper mark of the measuring standard should be below the level of the lowest mark of the vessel being tested. A two-way stop-cock makes it possible to empty the measuring standard, the total capacity of which may be only a fraction of that of the burette to be tested.

TABLE 1. BUOYANCY CONSTANTS (mg./ml.)

Difference in milligrams between the mass and the apparent weight of 1 milliliter of water weighed with brass weights (d = 8.4) in air at various temperatures and barometer readings (unreduced). A humidity of 50 per cent saturation is assumed. To find the weight of 1 milliliter of air under the conditions assumed in this table, multiply the buoyancy constant by 1.135 (42/37).

| Pressure | Temperature in Degrees Centigrade | | | |
|---|---|---|---|---|
| | 15 | 20 | 25 | 30 |
| 640 | 0.904 | 0.886 | 0.869 | 0.852 |
| 650 | 0.918 | 0.900 | 0.883 | 0.866 |
| 660 | 0.932 | 0.914 | 0.897 | 0.879 |
| 670 | 0.946 | 0.928 | 0.911 | 0.893 |
| 680 | 0.960 | 0.942 | 0.924 | 0.906 |
| 690 | 0.975 | 0.956 | 0.938 | 0.920 |
| 700 | 0.989 | 0.970 | 0.952 | 0.933 |
| 705 | 0.996 | 0.977 | 0.958 | 0.940 |
| 710 | 1.003 | 0.984 | 0.965 | 0.947 |
| 715 | 1.010 | 0.991 | 0.972 | 0.953 |
| 720 | 1.017 | 0.998 | 0.979 | 0.960 |
| 725 | 1.024 | 1.004 | 0.985 | 0.967 |
| 730 | 1.031 | 1.011 | 0.992 | 0.973 |
| 735 | 1.038 | 1.018 | 0.999 | 0.980 |
| 740 | 1.045 | 1.025 | 1.006 | 0.987 |
| 745 | 1.052 | 1.032 | 1.013 | 0.994 |
| 750 | 1.059 | 1.039 | 1.020 | 1.000 |
| 755 | 1.067 | 1.046 | 1.027 | 1.007 |
| 760 | 1.074 | 1.053 | 1.034 | 1.014 |
| 765 | 1.081 | 1.060 | 1.040 | 1.020 |
| 770 | 1.088 | 1.067 | 1.047 | 1.027 |
| 775 | 1.095 | 1.074 | 1.054 | 1.034 |
| 780 | 1.102 | 1.081 | 1.061 | 1.041 |

TABLE 2. DENSITY (in gms. per milliliter) OF WATER AT TEMPERATURES FROM 0° TO 102° C.

| Temp. °C. | Density | Temp. °C. | Density | Temp. °C. | Density |
|---|---|---|---|---|---|
| 0 | 0.99987 | 35 | 0.99406 | 70 | 0.97781 |
| 1 | 0.99993 | 36 | 0.99371 | 71 | 0.97723 |
| 2 | 0.99997 | 37 | 0.99336 | 72 | 0.97666 |
| 3 | 0.99999 | 38 | 0.99299 | 73 | 0.97607 |
| 4 | 1.00000 | 39 | 0.99262 | 74 | 0.97548 |
| 5 | 0.99999 | 40 | 0.99224 | 75 | 0.97489 |
| 6 | 0.99997 | 41 | 0.99186 | 76 | 0.97428 |
| 7 | 0.99993 | 42 | 0.99147 | 77 | 0.97368 |
| 8 | 0.99988 | 43 | 0.99107 | 78 | 0.97307 |
| 9 | 0.99981 | 44 | 0.99066 | 79 | 0.97245 |
| 10 | 0.99973 | 45 | 0.99024 | 80 | 0.97183 |
| 11 | 0.99963 | 46 | 0.98982 | 81 | 0.97120 |
| 12 | 0.99952 | 47 | 0.98940 | 82 | 0.97057 |
| 13 | 0.99940 | 48 | 0.98896 | 83 | 0.96994 |
| 14 | 0.99927 | 49 | 0.98852 | 84 | 0.96930 |
| 15 | 0.99913 | 50 | 0.98807 | 85 | 0.96865 |
| 16 | 0.99897 | 51 | 0.98762 | 86 | 0.96800 |
| 17 | 0.99880 | 52 | 0.98715 | 87 | 0.96734 |
| 18 | 0.99862 | 53 | 0.98669 | 88 | 0.96668 |
| 19 | 0.99843 | 54 | 0.98621 | 89 | 0.96601 |
| 20 | 0.99823 | 55 | 0.98573 | 90 | 0.96534 |
| 21 | 0.99802 | 56 | 0.98524 | 91 | 0.96467 |
| 22 | 0.99780 | 57 | 0.98478 | 92 | 0.96399 |
| 23 | 0.99756 | 58 | 0.98425 | 93 | 0.96330 |
| 24 | 0.99732 | 59 | 0.98375 | 94 | 0.96261 |
| 25 | 0.99707 | 60 | 0.98324 | 95 | 0.96192 |
| 26 | 0.99681 | 61 | 0.98272 | 96 | 0.96122 |
| 27 | 0.99654 | 62 | 0.98220 | 97 | 0.96051 |
| 28 | 0.99626 | 63 | 0.98167 | 98 | 0.95981 |
| 29 | 0.99597 | 64 | 0.98113 | 99 | 0.95909 |
| 30 | 0.99567 | 65 | 0.98059 | 100 | 0.95838 |
| 31 | 0.99537 | 66 | 0.98005 | 101 | 0.95765 |
| 32 | 0.99505 | 67 | 0.97950 | 102 | 0.95693 |
| 33 | 0.99473 | 68 | 0.97894 | | |
| 34 | 0.99440 | 69 | 0.97838 | | |
| 35 | 0.99406 | 70 | 0.97781 | | |

TABLE 3. APPARENT WEIGHT (in gms.) OF WATER IN AIR

(This table gives the apparent weight, for temperatures between 15° and 30° C., humidity 50 per cent, unreduced barometer reading 76 cm., of certain volumes of water weighed with brass weights. This table is based on the data given in Tables 1 and 2, and may be conveniently employed to determine definite volumes of water for calibrating instruments. The table assumes the air to be at the same temperature as the water.)

| Temp. in Degrees C. | 2000 ml. | 1000 ml. | 500 ml. | 400 ml. | 300 ml. | 250 ml. | 150 ml. |
|---|---|---|---|---|---|---|---|
| 15 | 1996.11 | 998.05 | 499.03 | 399.22 | 299.42 | 249.51 | 149.71 |
| 16 | 1995.80 | 997.90 | 498.95 | 399.16 | 299.37 | 249.48 | 149.68 |
| 17 | 1995.48 | 997.74 | 498.87 | 399.10 | 299.32 | 249.43 | 149.66 |
| 18 | 1995.13 | 997.56 | 498.78 | 399.03 | 299.27 | 249.39 | 149.63 |
| 19 | 1994.76 | 997.38 | 498.69 | 398.95 | 299.21 | 249.34 | 149.61 |
| 20 | 1994.36 | 997.18 | 498.59 | 398.87 | 299.15 | 249.30 | 149.58 |
| 21 | 1993.95 | 996.97 | 498.49 | 398.79 | 299.09 | 249.24 | 149.55 |
| 22 | 1993.51 | 996.76 | 498.38 | 398.70 | 299.03 | 249.19 | 149.51 |
| 23 | 1993.06 | 996.53 | 498.26 | 398.61 | 298.96 | 249.13 | 149.48 |
| 24 | 1992.58 | 996.29 | 498.15 | 398.52 | 298.89 | 249.07 | 149.44 |
| 25 | 1992.09 | 996.04 | 498.02 | 398.42 | 298.81 | 249.01 | 149.41 |
| 26 | 1991.57 | 995.79 | 497.89 | 398.31 | 298.74 | 248.95 | 149.37 |
| 27 | 1991.04 | 995.52 | 497.76 | 398.21 | 298.66 | 248.88 | 149.33 |
| 28 | 1990.49 | 995.24 | 497.62 | 398.10 | 298.57 | 248.81 | 149.29 |
| 29 | 1989.92 | 994.96 | 497.48 | 397.98 | 298.49 | 248.74 | 149.24 |
| 30 | 1989.33 | 994.66 | 497.33 | 397.87 | 298.40 | 248.67 | 149.20 |

## STANDARDIZATION OF WEIGHTS

Precision measurement of mass is the first requisite in accurate analysis. The chemist has at his command instruments for the measurement of mass which by far surpass in accuracy the major operations of his work. This is probably largely responsible for the negligence in the care of the balance and weights too frequently observed in the technical laboratory. It is often the case that the average technical laboratory uses analyses calculated to one decimal place more than warranted by the accuracy of the weights used. Assuming all other operations without error, an analysis made on a 1 gram sample and reported as 98.53% requires a weight accuracy of .0001 gram if the last figure is intended to have any significance.

Laboratories doing accurate analytical or research work should always be in possession of a set of standard weights and these weights should be used only in standardizing those in constant use. Where a large number of balances are used it is advisable to have two sets of standard weights, a Primary and a Secondary set, each ranging from 100 grams to 1 milligram. The Primary set is used exclusively for checking the Secondary set and is checked annually by the Bureau of Standards at Washington, D. C. The Secondary set is used for standardizing the weights assigned to the various balances. Where balances are used constantly, it is advisable to have the weights checked at least monthly against the Secondary set, and the Secondary likewise checked monthly against the Primary set. While this frequent checking may appear excessive, it is quite inexpensive insurance against errors which cannot easily be detected in any other way.

It is advisable to use one-piece gold-plated weights for the Primary Standard. The type designated Class M by the Bureau of Standards is very satisfactory. Lacquered brass weights are very satisfactory for general use.

The practice frequently observed in chemical laboratories of setting out the weights on the balance plate is very bad. While it expedites weighing, the chance of contaminating and changing the accuracy of the weights more than counterbalances the advantage of speed.

Students are frequently taught that it is not necessary for weights to bear true values so long as they are comparable to one another; that is, to bear true relation to each other. This contention holds good so long as all work done by the chemist is related to his balance. This condition does not exist in the majority of technical laboratories. The chemist frequently uses standard solutions made by use of other balances and for this reason his weighings must be comparable to others in the laboratory. This condition necessitates the standardization of all weights to true values.

Although there are several methods for weighing in use in the various technical laboratories, that of the double swing or vibration is probably the best for standardization of weights.

### Standardization

There are three methods for standardizing weights:

1. Standardizing the weights to true or absolute values.
2. Standardizing the weights to weigh true or absolute weights.
3. Standardizing the weights to bear true relation to each other.

The procedure followed in the first method is dependent upon the comparative arm lengths of the balance. If the arm lengths are equal the weights are standardized by direct weighing or balancing on the opposite pans. If unequal by substitution weighing or having both weights, when placed alternately on the left pan, balance a given mass on the right pan.

The standardization of the weights by the second method is independent of arm length. The weights are standardized by adjusting them so that when they are placed on the right pan they balance the standard weights of a similar denomination placed on the left pan.

In small laboratories where there is but one balance used for fine work, or for students' use, the third method is very satisfactory.

In the first two methods of standardization, each weight is standardized independently.

In all cases of two or more weights of one denomination, the second and third should be marked with one and two dots respectively.

It is, of course, assumed that high grade balances are used and are thoroughly understood by the chemist, and that in weighing, objects to be weighed are placed on the left pan.

**First Method.** — (Assuming the arm lengths unequal.) It is both convenient and time saving in this work to have an extra set of weights to use as counterpoises.

Place a standard 5 or 10 mgm. weight on the left pan and the 5 or 10 mgm. rider on the right beam. Adjust the weight of the rider until it balances the weight on the left pan when it is located at a point indicating that denomination. Remove both weights. Place the standard 100 gram weight on the left pan and balance it with the counterpoise set. Replace the standard with the 100 gram weight to be standardized and adjust the weight until it balances the counterpoise. Continue in this manner throughout the entire set.

In case the balance arms are equal the counterpoise set may be dispensed with and the set being standardized placed on the right pan. Of course when weights of absolute value are used on a balance having unequal arm lengths, corrections must be made on all weighings.

**Second Method.** — This method is the more practical since it is independent of arm length. However weights standardized in this way can only be used on the balance on which they have been standardized.

Place the standard 5 or 10 mgm. weight on the left pan and the 5 or 10 mgm. rider on the right beam, adjust the rider until it balances the weight on the left pan when it is on the point indicating the denomination of that weight. Remove both weights. Place the standard 100 gram weight on the left pan and the 100 gram weight to be standardized on the right pan. Adjust the weight until it balances the standard. Continue with all other weights in the same manner one at a time.

**Adjustment of Weights.** — Since it is not practical in commercial work to use corrections on weights, they should be adjusted when standardized. In the case of brass weights, by removing the top and either adding or removing granulated aluminum or lead (20–40 mesh) as required, and in the case of platinum fractional weights, fusing on gold shavings cut from foil or wire, if light, or removing platinum with a small file if heavy. When aluminum is used for fractional weights and one is found light, it is advisable to destroy it and replace with another.

When making the adjustment of the brass weight, the weight should be gripped with pieces of heavy linen cloth or chamois skin, never with the fingers. The metal should be added or removed with a pair of tweezers and the weight allowed to stand 15 minutes before final checking. While it is standing other weights may be adjusted. In this way little time is lost.

**Third Method.** — If the arms of the balance are equal the weights may be compared with each other. If, however, they are unequal the method of substitution must be used and another set of weights will be required. In the latter case the counterbalance weights are placed in the left pan and the set being standardized on the right.

The following method assumes the arm lengths equal or practically so.

Place the 5 or 10 mgm. weight on the left pan and the 5 or 10 mgm. rider on the right beam. Adjust the rider with fine emery cloth until it balances the weight when on the point indicating its denomination. Take a 10 mgm. weight from another box for use as a tare and call it T. Place T on the left pan and one of the 10 mgm. weights on the right and balance with the rider if necessary. Record the weight e.g. $0.01 = T + 0.0001$.

Replace the weight on the right with the other 10 mgm. weight and again balance.

Record the weight e.g. $0.01_2 = T + 0.0001$.

Replace the tare with the 20 mgm. weight and put both 10 mgm. weights on the right pan and balance. Record weights as follows:

$$0.02 = 0.01 + 0.01_2 + 0.0001$$

$$\text{or} \quad 0.02 = 2T + 0.0003$$

Replace the 20 mgm. weight with the 50 mgm. weight and place the 20 mgm. weight and tare on the right pan with the two ten mgm. weights. Balance and record the weights e.g.

$$0.05 = 0.02 + 0.01 + 0.01_2 + T + 0.0000$$

$$\text{or} \quad 0.05 = 5T + 0.0005$$

Place the 50 mgm. weight on the right pan and the 100 mgm. weight on the left pan. Balance and record the weight e.g.

$$0.10 = 0.05 + 0.02 + 0.01 + 0.01_2 + T - 0.0003$$

$$\text{or} \quad 0.10 = 10T + 0.0007$$

The remaining decigram and gram weights are tested in this manner and the results compiled as follows:

| Nominal Value | Value Found on Test | Values Using T = 0.01 | Corrected Using 1.0005 as Std. | Corrections |
|---|---|---|---|---|
| 0.01 | T + 0.0001 | 0.0101 | 0.0100 | + 0.0001 |
| $0.01_2$ | T + 0.0001 | 0.0101 | 0.0100 | + 0.0001 |
| 0.02 | 2 T + 0.0003 | 0.0203 | 0.0200 | + 0.0003 |
| 0.05 | 5 T + 0.0005 | 0.0505 | 0.0500 | + 0.0005 |
| 0.10 | 10 T + 0.0007 | 0.1007 | 0.1001 | + 0.0006 |
| $0.10_2$ | 10 T + 0.0006 | 0.1006 | 0.1001 | + 0.0005 |
| 0.20 | 20 T + 0.0007 | 0.2007 | 0.2001 | + 0.0006 |
| 0.50 | 50 T + 0.0004 | 0.5004 | 0.5003 | + 0.0001 |
| 1.00 | 100 T + 0.0005 | 1.0005 | 1.0005 | + 0.0000 |
| 2.00 | 200 T + 0.0006 | 2.0006 | 2.0010 | − 0.0004 |
| $2.00_2$ | 200 T + 0.0009 | 2.0009 | 2.0010 | − 0.0001 |
| etc. | | | | |

**Effect of Buoyancy.** — In making accurate weighings the buoyant effect of air on the weight and mass being weighed must be considered. When the mass being weighed has a specific gravity differing with that of the weights the buoyancy of the air on the two masses will affect the accuracy of the weighing. Thus the weighing of a 1 gram sample of Potassium Chloride with brass weights without correction for buoyancy results in an error of .00046 grams or approximately .05%.

The following formula may be used in making this correction for general work carried on under normal conditions.

$$\text{Correct weight} = W + .0012 \left( \frac{W}{S} - \frac{W}{S_1} \right)$$

Where W = the apparent weight of the object, S and $S_1$ the specific gravities of the object and weights respectively.

.0012 is the weight of 1 cc. of air at normal laboratory conditions.

The specific gravities of metal generally used in weights are — Platinum 21.5, Brass 8.4 and Aluminum 2.7.

**Precision and Tolerances of Weights.** — The following is a table of the Precision of Corrections and Tolerances of Class S analytical weights issued by the U. S. Bureau of Standards, Washington, D. C. While it is quite evident that the Precision of Correction is beyond the accuracy of a 1/10 mgm. or even a 1/20 mgm. balance, it is however advisable to standardize the weights to the limit of sensitiveness of the balance.

| *Denomination* | *Tolerance* | *Precision of Correction* |
|---|---|---|
| 100 grams | 0.5 mgm. | 0.1 mgm. |
| 50 | 0.3 | 0.1 |
| 20 | 0.2 | 0.1 |
| 10 | 0.15 | 0.05 |
| 5 | 0.15 | 0.05 |
| 2 | 0.1 | 0.05 |
| 1 | 0.1 | 0.05 |
| 500 mgms. | 0.05 | 0.01 |
| 200 | 0.05 | 0.01 |
| 100 | 0.05 | 0.01 |
| 50 | 0.03 | 0.01 |
| 20 | 0.03 | 0.01 |
| 10 | 0.02 | 0.01 |
| 5 | 0.02 | 0.01 |
| 2 | 0.01 | 0.01 |
| 1 | 0.01 | 0.01 |

# TABLES AND USEFUL DATA

## I.—INTERNATIONAL ATOMIC WEIGHTS, 1921

| | Symbol. | Atomic Weight. | | Symbol | Atomic Weight. |
|---|---|---|---|---|---|
| Aluminum | Al | 27.1 | Neodymium | Nd | 144.3 |
| Antimony | Sb | 120.2 | Neon | Ne | 20.2 |
| Argon | A | 39.9 | Nickel | Ni | 58.68 |
| Arsenic | As | 74.96 | Niton (radium emanation) | Nt | 222.4 |
| Barium | Ba | 137.37 | Nitrogen | N | 14.008 |
| Bismuth | Bi | 208.0 | Osmium | Os | 190.9 |
| Boron | B | 10.9 | Oxygen | O | 16.00 |
| Bromine | Br | 79.92 | Palladium | Pd | 106.7 |
| Cadmium | Cd | 112.40 | Phosphorus | P | 31.04 |
| Caesium | Cs | 132.81 | Platinum | Pt | 195.2 |
| Calcium | Ca | 40.07 | Potassium | K | 39.10 |
| Carbon | C | 12.005 | Praseodymium | Pr | 140.9 |
| Cerium | Ce | 140.25 | Radium | Ra | 226.0 |
| Chlorine | Cl | 35.46 | Rhodium | Rh | 102.9 |
| Chromium | Cr | 52.0 | Rubidium | Rb | 85.45 |
| Cobalt | Co | 58.97 | Ruthenium | Ru | 101.7 |
| Columbium | Cb | 93.1 | Samarium | Sa | 150.4 |
| Copper | Cu | 63.57 | Scandium | Sc | 45.1 |
| Dysprosium | Dy | 162.5 | Selenium | Se | 79.2 |
| Erbium | Er | 167.7 | Silicon | Si | 28.3 |
| Europium | Eu | 152.0 | Silver | Ag | 107.88 |
| Fluorine | F | 19.0 | Sodium | Na | 23.00 |
| Gadolinium | Gd | 157.3 | Strontium | Sr | 87.63 |
| Gallium | Ga | 70.1 | Sulphur | S | 32.06 |
| Germanium | Ge | 72.5 | Tantalum | Ta | 181.5 |
| Glucinum | Gl | 9.1 | Tellurium | Te | 127.5 |
| Gold | Au | 197.2 | Terbium | Tb | 159.2 |
| Helium | He | 4.00 | Thallium | Tl | 204.0 |
| Holmium | Ho | 163.5 | Thorium | Th | 232.15 |
| Hydrogen | H | 1.008 | Thulium | Tm | 168.5 |
| Indium | In | 114.8 | Tin | Sn | 118.7 |
| Iodine | I | 126.92 | Titanium | Ti | 48.1 |
| Iridium | Ir | 193.1 | Tungsten | W | 184.0 |
| Iron | Fe | 55.84 | Uranium | U | 238.2 |
| Krypton | Kr | 82.92 | Vanadium | V | 51.0 |
| Lanthanum | La | 139.0 | Xenon | Xe | 130.2 |
| Lead | Pb | 207.20 | Ytterbium (Neoytterbium) | Yb | 173.5 |
| Lithium | Li | 6.94 | Yttrium | Yt | 89.33 |
| Lutecium | Lu | 175.0 | Zinc | Zn | 65.37 |
| Magnesium | Mg | 24.32 | Zirconium | Zr | 90.6 |
| Manganese | Mn | 54.93 | | | |
| Mercury | Hg | 200.6 | | | |
| Molybdenum | Mo | 96.0 | | | |

## TABLES AND USEFUL DATA

### II.—MELTING-POINTS OF THE CHEMICAL ELEMENTS[1]

Reproduced from Circular No. 35 (2d edition) of U. S. Bureau of Standards.

| *Element.* | C. | F. |
|---|---|---|
| Helium | <−271 | <−456 |
| Hydrogen | −259 | −434 |
| Neon | −253? | −423 |
| Fluorine | −223 | −369 |
| Oxygen | −218 | −360 |
| Nitrogen | −210 | −346 |
| Argon | −188 | −306 |
| Krypton | −169 | −272 |
| Xenon | −140 | −220 |
| Chlorine | −101.5 | −150.7 |
| Mercury | − 38.9 | −38.0 |
| Bromine | − 7.3 | +18.9 |
| Caesium | + 26 | 79 |
| Gallium | 30 | 86 |
| Rubidium | 38 | 100 |
| Phosphorus | 44 | 111.2 |
| Potassium | 62.3 | 144 |
| Sodium | 97.5 | 207.5 |
| Iodine | 113.5 | 236.3 |
| Sulphur | $S_I$ 112.8 | 235.0 |
| | $S_{II}$ 119.2 | 246.6 |
| | $S_{III}$ 106.8 | 224.2 |
| Indium | 155 | 311 |
| Lithium | 186 | 367 |
| Selenium | 217–220 | 422–428 |
| TIN | 231.9 | 449.4 |
| Bismuth | 271 | 520 |
| Thallium | 302 | 576 |
| CADMIUM | 320.9 | 609.6 |
| LEAD | 327.4 | 621.3 |
| ZINC | 419.4 | 786.9 |
| Tellurium | 452 | 846 |
| ANTIMONY | 630.0 | 1166 |
| Cerium | 640 | 1184 |
| Magnesium | 651 | 1204 |
| ALUMINUM | 658.7 | 1217.7 |
| Radium | 700 | 1292 |
| Calcium | 810 | 1490 |
| Lanthanum | 810? | 1490 |
| Strontium | >Ca<Ba? | |

| *Element.* | C. | F. |
|---|---|---|
| Neodymium | 840? | 1544 |
| Arsenic | 850? | 1562 |
| Barium | 850 | 1562 |
| Praseodymium | 940? | 1724 |
| Germanium | 958 | 1756 |
| SILVER | 960.5 | 1761 |
| GOLD | 1063.0 | 1945.5 |
| COPPER | 1083.0 | 1981.5 |
| Manganese | 1260 | 2300 |
| Samarium | 1300–1400 | 2370–2550 |
| Beryllium (glucinum) | 1350? | 2462 |
| Scandium | ? | |
| Silicon | 1420 | 2588 |
| NICKEL | 1452 | 2646 |
| Cobalt | 1480 | 2696 |
| Yttrium | 1490 | 2714 |
| Chromium | 1520 | 2768 |
| IRON | 1530 | 2786 |
| PALLADIUM | 1549 | 2820 |
| Zirconium | 1700? | 3090 |
| Columbium (Niobium) | 1700? | 3090 |
| Thorium | >1700 | >3090 |
| | <Pt | <Pt |
| Vanadium | 1720 | 3128 |
| PLATINUM | 1755 | 3191 |
| Ytterbium | ? | |
| Titanium | 1800 | 3272 |
| Uranium | <1850 | <3362 |
| Rhodium | 1950 | 3542 |
| Boron | 2200–2500? | 4000–4500 |
| Iridium | 2350? | 4262 |
| Ruthenium. | 2450? | 4442 |
| Molybdenum | 2500? | 4500 |
| Osmium | 2700? | 4900 |
| Tantalum | 2850 | 5160 |
| TUNGSTEN | 3000 | 5430 |
| Carbon | >3600 for p. = 1 at. | >6500 for p. = 1 at. |

### III. OTHER TEMPERATURE STANDARDS

*Temperatures of Flames.*[2]

| | Cent. | Deg. of Accuracy. |
|---|---|---|
| Bunsen, open | 1100 | Within 100° C.[3] |
| Meker | 1500[1] | |
| Petrol blow lamp | 1600[1] | |
| Oxyhydrogen with $H_2+O$ | 2420 | Within 100° C. |
| Oxyacetylene | 2400[1] | |
| Thermat | 2500 | |
| Electric arc | 3500 | Within 150° C. |
| Sun | 6000 | Within 500° C. |

[1] Metallurgical and Chemical Engineering, Vol. XIII, No. 5, May, 1915.

[2] Measurement of High Temperatures, G. K. Burgess and H. Le Chatelier.

[3] Pyrometer tests of the open Bunsen flame gave temperatures ranging from 1000° to 1100° C.

## TABLES AND USEFUL DATA

### III.—OTHER TEMPERATURE STANDARDS (Continued)

*Approximate Temperatures by Colors.*

| | Cent. | Fahr. |
|---|---|---|
| First visible red | 525 | 977 |
| Dull red | 700 | 1292 |
| Cherry red | 900 | 1652 |
| Dull orange | 1100 | 2012 |
| White | 1300 | 2372 |
| Dazzling white | 1500 | 2732 |

| Substance. | Phenomenon. | C. | F. | Variation with pressure (pressure in mm. of Hg.) |
|---|---|---|---|---|
| Oxygen | Boiling | −183.0 | −297.4 | C. °−183.0+0.01258 (p. 760) −0.0000079 (p. 760) |
| Carbon dioxide | Sublimation in inert liquid | − 78.5 | −109.3 | C. °= −78.5+0.017 (p. 760) |
| Sodium sulphate $Na_2SO_4+10H_2O$ | Transformation into anhydrous salt | 32.384 | 90.291 | |
| Water | Boiling | 100 | 212 | C. °−100+0.03670 (p. 760) −0.00002046 (p. 760) |
| Naphthalene | Boiling | 217.96 | 423.73 | C. °=217.96+0.058 (p. 760) |
| Benzophenone | Boiling | 305.9 | 582.6 | C. °−305.9+0.063 (p. 760) |
| Sulphur | Boiling | 444.6 | 832.3 | C. °=444.6+0.0908 (p. 760) −0.000047 (p. 760) |
| $Ag_2Cu_2$ | Eutectic Freezing | 779 | 1434 | |
| Sodium chloride | Freezing | 801 | 1472 | |

### IV.—ELECTROMOTIVE ARRANGEMENT OF THE ELEMENTS

Each element is positive to the element placed after it and negative to the element placed above.

| | | | | |
|---|---|---|---|---|
| 1. Cs | 14. Al | 27. Ge | 40. Os | 53. Mo |
| 2. Rb | 15. Zr | 28. In | 41. Au | 54. V |
| 3. K | 16. Th | 29. Ga | 42. H | 55. Cr |
| 4. Na | 17. Ce | 30. Bi | 43. Sn | 56. As |
| 5. Li | 18. Di | 31. U | 44. Si | 57. P |
| 6. Ba | 19. La | 32. Cu | 45. Ti | 58. Se |
| 7. Sr | 20. Mn | 33. Ag | 46. Cb | 59. I |
| 8. Ca | 21. Zn | 34. Hg | 47. Ta | 60. Br |
| 9. Mg | 22. Fe | 35. Pd | 48. Te | 61. Cl |
| 10. Be | 23. Ni | 36. Ru | 49. Sb | 62. F |
| 11. Yt | 24. Co | 37. Rh | 50. C | 63. N |
| 12. Er | 25. Cd | 38. Pt | 51. Bo | 64. S |
| 13. Sc | 26. Pb | 39. Ir | 52. W | 65. O |

## TABLES AND USEFUL DATA

### V.—SPECIFIC GRAVITY OF GASES*

| Name. | Formula. | Molecular Weight. | Specific Gravity, Air = 1. | | Weight in Grams of 1 Liter at 0°, 760 mm. at Sea Level, Lat. 45°.[2] |
|---|---|---|---|---|---|
| | | | Calculated.[1] | Observed. | |
| Acetylene | $C_2H_2$ | 26.026 | 0.8993 | 0.9056 | 1.1624 |
| Air | | | 1.0000 | | 1.2926 |
| Ammonia | $NH_3$ | 17.034 | 0.5856 | 0.5971 | 0.7608 |
| Argon | A | 39.88 | 1.3780 | 1.379 | 1.7812 |
| Arsine | $AsH_3$ | 77.984 | 2.6933 | 2.695 | 3.4830 |
| Bromine | $Br_2$ | 159.84 | 5.5230 | 5.524(227.9°) | 7.1390 |
| Butane | $C_4H_{10}$ | 58.10 | 2.0075 | 2.01 | 2.5949 |
| Carbon dioxide | $CO_2$ | 44.005 | 1.5205 | 1.52908 | 1.9654 |
| Carbon monoxide | CO | 28.005 | 0.9677 | 0.96716 | 1.2508 |
| Carbon oxysulphide | COS | 60.065 | 2.0754 | 2.1046 | 2.6827 |
| Chlorine | $Cl_2$ | 70.92 | 2.4505 | 2.4901 | 3.1675 |
| Cyanogen | $C_2N_2$ | 52.03 | 1.7977 | 1.8064 | 2.3338 |
| Ethane | $C_2H_6$ | 30.058 | 1.0386 | 1.0494 | 1.3425 |
| Ethylene | $C_2H_4$ | 28.042 | 0.9689 | 0.9852 | 1.2524 |
| Fluorine | $F_2$ | 38.0 | 1.3130 | 1.26 | 1.6972 |
| Helium | He | 4.00 | 0.1382 | 0.131 | 0.1786 |
| Hydrobromic acid | HBr | 80.928 | 2.7963 | 2.71 | 3.6145 |
| Hydrochloric acid | HCl | 36.468 | 1.2601 | 1.2681 | 1.6288 |
| Hydrofluoric acid | HF | 20.008 | 0.6913 | 0.7126 | 0.8936 |
| Hydroiodic acid | HI | 127.928 | 4.4203 | 4.3757 | 5.7137 |
| Hydrogen | $H_2$ | 2.016 | 0.06965 | 0.06952 | 0.09004 |
| Hydrogen selenide | $H_2Se$ | 81.216 | 2.8063 | 2.795 | 3.6274 |
| Hydrogen sulphide | $H_2S$ | 34.076 | 1.1774 | 1.1906 | 1.5220 |
| Hydrogen telluride | $H_2Te$ | 129.516 | 4.4752 | 4.489 | 5.7846 |
| Krypton | Kr | 82.92 | 2.8252 | 2.868 | 3.7035 |
| Methane | $CH_4$ | 16.037 | 0.5541 | 0.5545 | 0.7163 |
| Neon | Ne | 20.2 | 0.6980 | 0.6963 | 0.9022 |
| Nitric oxide | NO | 30.01 | 1.0370 | 1.0367 | 1.3404 |
| Nitrous oxide | $N_2O$ | 44.02 | 1.5210 | 1.5298 | 1.9661 |
| Nitrogen | $N_2$ | 28.02 | 0.9682 | 0.96737 | 1.2515 |
| atmospheric | $N_2$+A etc. | | | 0.97209 | 1.25718 |
| Nitrogen dioxide | $NO_2$ | 46.01 | 1.5898 | 1.60(135°) | 2.0550 |
| " " | $N_2O_4$ | 92.02 | 3.1788 | 2.65(26.7°) | 4.1099 |
| Nitrosyl chloride | NOCl | 65.47 | 2.2622 | 2.31 | 2.9241 |
| Oxygen | $O_2$ | 32.00 | 1.1057 | 1.1053 | 1.4292 |
| Phosphine | $PH_3$ | 34.064 | 1.1770 | 1.1829 | 1.5214 |
| Propylene | $C_3H_6$ | 42.063 | 1.4534 | 1.498 | 1.8787 |
| Silicon fluoride | $SiF_4$ | 104.3 | 3.6039 | 3.60 | 4.6584 |
| Sulphur dioxide | $SO_2$ | 64.06 | 2.2135 | 2.2638 | 2.8611 |
| Xenon | X | 130.2 | 4.4988 | 4.526 | 5.8152 |

*D. Van Nostrand Chemical Annual.—Olsen.

[1] Obtained by dividing the weight of one liter of the gas by 1.2926 (*i.e.*, by the weight of one liter of air).

[2] Obtained by multiplying $\frac{1}{2}$ the molecular weight of the gas by $\frac{1}{16} \times 1.429234$ (*i.e.*, by $\frac{1}{16} \times$ weight of one liter of oxygen).

## TABLES AND USEFUL DATA

### VI.—VAPOR TENSION OF WATER IN MILLIMETERS OF MERCURY −2° TO −36° C.

According to Regnault, Broch, and Weibe

| °C. | 0 | .1 | .2 | .3 | .4 | .5 | .6 | .7 | .8 | .9 |
|---|---|---|---|---|---|---|---|---|---|---|
| | mm. | mm. | mm. | mm. | mm. | mm. | mm. | mm. | mm. | mm. |
| −2 | 3.958 | 3.929 | 3.900 | 3.872 | 3.844 | 3.815 | 3.787 | 3.760 | 3.732 | 3.705 |
| −1 | 4.258 | 4.227 | 4.197 | 4.166 | 4.136 | 4.106 | 4.076 | 4.046 | 4.016 | 3.987 |
| −0 | 4.579 | 4.546 | 4.513 | 4.481 | 4.448 | 4.416 | 4.384 | 4.352 | 4.321 | 4.289 |
| 0 | 4.579 | 4.612 | 4.646 | 4.679 | 4.713 | 4.747 | 4.782 | 4.816 | 4.851 | 4.886 |
| 1 | 4.921 | 4.957 | 4.992 | 5.028 | 5.064 | 5.101 | 5.137 | 5.174 | 5.211 | 5.248 |
| 2 | 5.286 | 5.324 | 5.362 | 5.400 | 5.438 | 5.477 | 5.516 | 5.555 | 5.595 | 5.635 |
| 3 | 5.675 | 5.715 | 5.755 | 5.796 | 5.837 | 5.878 | 5.920 | 5.961 | 6.003 | 6.046 |
| 4 | 6.088 | 6.131 | 6.174 | 6.217 | 6.261 | 6.305 | 6.349 | 6.393 | 6.438 | 6.483 |
| 5 | 6.528 | 6.574 | 6.620 | 6.666 | 6.712 | 6.759 | 6.806 | 6.853 | 6.901 | 6.949 |
| 6 | 6.997 | 7.045 | 7.094 | 7.143 | 7.192 | 7.242 | 7.292 | 7.342 | 7.392 | 7.443 |
| 7 | 7.494 | 7.546 | 7.598 | 7.650 | 7.702 | 7.755 | 7.808 | 7.861 | 7.914 | 7.968 |
| 8 | 8.023 | 8.077 | 8.132 | 8.187 | 8.243 | 8.299 | 8.355 | 8.412 | 8.469 | 8.526 |
| 9 | 8.584 | 8.642 | 8.700 | 8.759 | 8.818 | 8.877 | 8.937 | 8.997 | 9.057 | 9.118 |
| 10 | 9.179 | 9.240 | 9.302 | 9.364 | 9.427 | 9.490 | 9.553 | 9.616 | 9.680 | 9.745 |
| 11 | 9.810 | 9.875 | 9.940 | 10.006 | 10.072 | 10.139 | 10.206 | 10.274 | 10.342 | 10.410 |
| 12 | 10.479 | 10.548 | 10.617 | 10.687 | 10.757 | 10.828 | 10.899 | 10.970 | 11.042 | 11.114 |
| 13 | 11.187 | 11.260 | 11.333 | 11.407 | 11.481 | 11.556 | 11.631 | 11.706 | 11.782 | 11.859 |
| 14 | 11.936 | 12.013 | 12.091 | 12.169 | 12.247 | 12.326 | 12.406 | 12.486 | 12.566 | 12.647 |
| 15 | 12.728 | 12.810 | 12.892 | 12.974 | 13.057 | 13.141 | 13.225 | 13.309 | 13.394 | 13.480 |
| 16 | 13.565 | 13.651 | 13.738 | 13.825 | 13.913 | 14.001 | 14.090 | 14.179 | 14.269 | 14.359 |
| 17 | 14.450 | 14.541 | 14.632 | 14.724 | 14.817 | 14.910 | 15.003 | 15.097 | 15.192 | 15.287 |
| 18 | 15.383 | 15.479 | 15.575 | 15.672 | 15.770 | 15.868 | 15.967 | 16.066 | 16.166 | 16.266 |
| 19 | 16.367 | 16.469 | 16.571 | 16.673 | 16.776 | 16.880 | 16.984 | 17.088 | 17.193 | 17.299 |
| 20 | 17.406 | 17.513 | 17.620 | 17.728 | 17.837 | 17.947 | 18.057 | 18.167 | 18.278 | 18.390 |
| 21 | 18.503 | 18.616 | 18.729 | 18.844 | 18.959 | 19.074 | 19.190 | 19.307 | 19.424 | 19.542 |
| 22 | 19.661 | 19.780 | 19.900 | 20.021 | 20.142 | 20.264 | 20.386 | 20.510 | 20.634 | 20.758 |
| 23 | 20.883 | 21.010 | 21.137 | 21.264 | 21.393 | 21.522 | 21.652 | 21.782 | 21.913 | 22.045 |
| 24 | 22.178 | 22.311 | 22.446 | 22.581 | 22.716 | 22.853 | 22.990 | 23.128 | 23.266 | 23.406 |
| 25 | 23.546 | 23.686 | 23.828 | 23.970 | 24.113 | 24.257 | 24.401 | 24.547 | 24.693 | 24.839 |
| 26 | 24.987 | 25.135 | 25.284 | 25.434 | 25.584 | 25.736 | 25.888 | 26.041 | 26.195 | 26.349 |
| 27 | 26.505 | 26.661 | 26.818 | 26.976 | 27.134 | 27.294 | 27.454 | 27.615 | 27.777 | 27.939 |
| 28 | 28.103 | 28.267 | 28.432 | 28.599 | 28.766 | 28.933 | 29.102 | 29.271 | 29.442 | 29.613 |
| 29 | 29.785 | 29.958 | 30.132 | 30.307 | 30.482 | 30.659 | 30.836 | 31.015 | 31.194 | 31.374 |
| 30 | 31.555 | 31.737 | 31.919 | 32.103 | 32.288 | 32.473 | 32.660 | 32.847 | 33.036 | 33.225 |
| 31 | 33.416 | 33.607 | 33.799 | 33.992 | 34.187 | 34.382 | 34.578 | 34.775 | 34.973 | 35.172 |
| 32 | 35.372 | 35.573 | 35.775 | 35.978 | 36.182 | 36.387 | 36.593 | 36.800 | 37.008 | 37.217 |
| 33 | 37.427 | 37.638 | 37.851 | 38.064 | 38.278 | 38.493 | 38.710 | 38.927 | 39.146 | 39.365 |
| 34 | 39.586 | 39.807 | 40.030 | 40.254 | 40.479 | 40.705 | 40.933 | 41.161 | 41.390 | 41.621 |
| 35 | 41.583 | 42.085 | 42.319 | 42.554 | 42.791 | 43.028 | 43.266 | 43.506 | 43.747 | 43.989 |

## TABLES AND USEFUL DATA

### VII.—USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS *

| Substance. | Formula. | Molecular or Atomic Weight. | Normal Coefficient 1 c.c. = gm. | Solubility in 100 Gms. Water. | Indicator. |
|---|---|---|---|---|---|
| Acetic acid | $HC_2H_3O_2$ | 60.04 | .06004 | | |
| anhydride | $(CH_3CO)_2O$ | 102.07 | .051035 | | |
| Aluminium | Al | 27.10 | .009033 | | |
| chloride | $Al_2Cl_6$ | 266.96 | .04449 | 69.87[15°] | P. |
| chloride | $Al_2Cl_6 \cdot 12H_2O$ | 483.15 | .08053 | 40 | P. |
| oxide | $Al_2O_3$ | 102.20 | .01703 | insol. | |
| phosphate | $AlPO_4$ | 122.14 | .04071 | | |
| sulphate | $Al_2(SO_4)_3$ | 342.38 | .05706 | 36.1[20°] | P. |
| sulphate | $Al_2(SO_4)_3 18H_2O$ | 666.67 | .11111 | 87 | P. |
| Ammonia | $NH_3$ | 17.03 | .01703 | ..... | M. |
| Ammonium | $NH_4$ | 18.04 | .01804 | ..... | M. |
| chloride | $NH_4Cl$ | 53.50 | .05350 | 29.4[0°] | M. |
| hydroxide | $NH_4OH$ | 35.05 | .03505 | ..... | M. |
| nitrate | $NH_4NO_3$ | 80.05 | .08005 | 118[0°] | M. |
| oxalate | $(NH_4)_2C_2O_4 \cdot H_2O$ | 142.11 | .07105[13] | | |
| sulphate | $(NH_4)_2SO_4$ | 132.14 | .06607 | 71[0°] | M. |
| Antimony | Sb | 120.20 | .06010 | | |
| chloride (tri) | $SbCl_3$ | 226.58 | .11329[3] | | |
| chloride (penta) | $SbCl_5$ | 297.50 | .14875[3] | | |
| oxide (tri) | $Sb_2O_3$ | 288.40 | .07210[3] | | |
| oxide (penta) | $Sb_2O_5$ | 320.40 | .08010[3] | | |
| Arsenic | As | 74.96 | .03748 | | |
| oxide | $As_2O_5$ | 229.92 | .03832 [1] | 150 | |
| oxide | $As_2O_6$ | 229.92 | .05748 [3] | | |
| Arsenious oxide | $As_2O_3$ | 197.92 | .03299 | 1.7[16°] | |
| Arsenious oxide | $As_2O_3$ | 197.92 | .04948 [3] | 1.7[16°] | |
| Barium | Ba | 137.37 | .068685 | | |
| carbonate | $BaCO_3$ | 197.37 | .098685 | .0022[20°] | M. |
| chloride | $BaCl_2$ | 208.29 | .104145 | 30.9[0°] | |
| chloride | $BaCl_2 2H_2O$ | 244.32 | .12216 | 36.2[0°] | |
| hydroxide | $Ba(OH)_2$ | 171.38 | .08569 | | |
| hydroxide | $Ba(OH)_2 8H_2O$ | 315.51 | .15775 | 5.15[15°] | |
| oxalate | $BaC_2O_4 \cdot H_2O$ | 243.40 | .12170 | | |
| oxide | BaO | 153.37 | .076685 | 1.5[0°] | |
| sulphate | $BaSO_4$ | 233.43 | .11672 | .000172[0°] | |
| sulphite | $BaSO_3$ | 217.43 | .10872 | | |
| peroxide | $BaO_2$ | 169.37 | .08469 [3] | insol. | |
| Boric acid | $H_3BO_3$ | 61.92 | .06192 | | |
| Bromine | Br | 79.92 | .07992 | 4.17[0°] | |
| Cadmium carbonate | $CdCO_3$ | 172.405 | .08620 | insol. | |
| chloride | $CdCl_2$ | 183.32 | .09166 | 140[20°] | |
| chloride | $CdCl_2 2H_2O$ | 219.35 | .109675 | 168[20°] | |
| sulphide | CdS | 144.46 | .07223 | insol. | |
| Calcium | Ca | 40.07 | .020035 | | |
| acetate | $Ca(C_2H_3O_2)_2$ | 158.14 | .07907 | | |
| bicarbonate | $Ca(HCO_3)_2$ | 162.10 | .08105 | | |
| carbonate | $CaCO_3$ | 100.075 | .050037 | .0013 | M. |
| chloride | $CaCl_2$ | 110.99 | .055495 | 59.5[0°] | |
| chloride | $CaCl_2 6H_2O$ | 219.09 | .109543 | 117.4[0°] | |
| fluoride | $CaF_2$ | 78.07 | .039035 | | |
| hydroxide | $Ca(OH)_2$ | 74.09 | .037045 | 17[0°] | |
| oxalate | $CaC_2O_4 \cdot H_2O$ | 146.10 | .07305 | | |

[1] Precipitation reagents. [2] Acids and bases. [3] Oxidizing and reducing agents.
M. Methyl orange. P. Phenolphthalein. Temp. C.

* Compiled and arranged by R. M. Meiklejohn.

## TABLES AND USEFUL DATA

### VII.—USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS (Continued)

| Substance. | Formula. | Molecular or Atomic Weight. | Normal Coefficient 1 c.c. = gm. | Solubility in 100 Gms. Water. | Indicator. |
|---|---|---|---|---|---|
| Calcium oxide | $CaO$ | 56.07 | .028035 | .13° | |
| sulphate | $CaSO_4$ | 136.13 | .06807 | .179° | |
| sulphide | $CaS$ | 72.13 | .03607 | .15[10]° | |
| Carbon | $C$ | 12.005 | .003001 | insol. | |
| dioxide | $CO_2$ | 44.005 | .022003[1] | 179.67 cc.° | |
| dioxide | $CO_2$ | 44.005 | .044005[2] | " | P. |
| Chlorine | $Cl$ | 35.46 | .03546 | 150 cc.° | |
| Chromic anhydride | $CrO_3$ | 100.00 | .033333[3] | 163.40° | |
| oxide | $Cr_2O_3$ | 152.00 | .025333[3] | insol. | |
| Citric acid | $H_4C_6H_3O_7$ | 192.09 | .06403 | 133. | |
| Cobalt | $Co$ | 58.97 | .029485 | | |
| Copper | $Cu$ | 63.57 | .031785 | | |
| oxide | $CuO$ | 79.57 | .07957 | | |
| sulphate | $CuSO_4$ | 159.63 | .15963 | 20° | |
| sulphate | $CuSO_45H_2O$ | 249.71 | .24971 | 31.61° | |
| sulphide | $CuS$ | 95.63 | .047815 | .000033 | |
| Cyanogen | $CN$ | 26.013 | .026013 | | |
| Ferric oxide | $Fe_2O_3$ | 159.68 | .07984[3] | | |
| phosphate | $FePO_4{\cdot}4H_2O$ | 222.94 | .07431 | | |
| Ferrous oxide | $FeO$ | 71.84 | .07184[3] | insol. | |
| sulphate | $FeSO_4$ | 151.90 | .15190[3] | | |
| sulphate | $FeSO_47H_2O$ | 278.01 | .27801[3] | 32.8° | |
| ammon'm sulphate | $FeSO_4(NH_4)_2SO_46H_2O$ | 392.14 | .39214 | 18° | |
| Formic acid | $HCOOH$ | 46.02 | .04602 | | |
| Hydrobromic acid | $HBr$ | 80.93 | .08093 | 221.2° | |
| Hydrochloric acid | $HCl$ | 36.47 | .03647 | 82.5[10]° | |
| Hydrocyanic acid | $HCN$ | 27.02 | .02702 | | |
| Hydrofluoric acid | $HF$ | 20.01 | .02001 | 264 | |
| Hydrofluosilicic acid | $H_2SiF_6$ | 144.32 | .02405[2] | | |
| Hydroiodic acid | $HI$ | 127.93 | .12793 | | |
| Hydrogen peroxide | $H_2O_2$ | 34.016 | .017008 | | |
| Hydrogen sulphide | $H_2S$ | 34.076 | .017038 | 437 cc.° | |
| Iodine | $I$ | 126.92 | .12692 | .0182[11]° | |
| Iron | $Fe$ | 55.84 | .05584 | | |
| Lead | $Pb$ | 207.20 | .10360 | | |
| carbonate | $PbCO_3$ | 267.205 | .13360 | .00168 | M. |
| chromate | $PbCrO_4$ | 323.20 | .16160 | .00002[18]° | |
| oxide | $PbO$ | 223.20 | .11160 | | |
| peroxide | $PbO_2$ | 239.20 | .11960 | | |
| sulphate | $PbSO_4$ | 303.26 | .15163 | | |
| sulphide | $PbS$ | 239.26 | .11963 | .0001 | |
| sulphite | $PbSO_3$ | 287.26 | .14363[1] | | |
| Magnesium | $Mg$ | 24.32 | .01216 | | |
| carbonate | $MgCO_3$ | 84.32 | .04216 | .0106 | |
| chloride | $MgCl_2$ | 95.24 | .04762 | 52.2° | M. |
| chloride | $MgCl_26H_2O$ | 203.34 | .10167 | 167 | M. |
| oxide | $MgO$ | 40.32 | .02016 | 00062 | M. |
| sulphate | $MgSO_4$ | 120.38 | .06019 | 26.9° | M. |
| sulphate | $MgSO_47H_2O$ | 246.49 | .123245 | 76.9° | M. |
| Malic acid | $H_2C_4H_4O_5$ | 134.07 | .06703 | | |
| Manganese | $Mn$ | 54.93 | .027465 | | |
| chloride | $MnCl_2$ | 125.85 | .062925 | 62.16[10]° | |
| peroxide | $MnO_2$ | 86.93 | .043465 | insol. | |

[1] Precipitation reagents. [2] Acids and bases. [3] Oxidizing and reducing agents.
M. Methyl orange. P. Phenolphthalein. Temp. C.

## TABLES AND USEFUL DATA

### VII.—USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS (Continued)

| Substance. | Formula. | Molecular or Atomic Weight. | Normal Coefficient 1 c.c. = gm. | Solubility in 100 Gms. Water. | Indicator. |
|---|---|---|---|---|---|
| Manganese sulphate | $MnSO_4$ | 150.99 | .075495 | 53.2° | |
| Mercuric chloride | $HgCl_2$ | 271.52 | .13576 | 5.73° | |
| Mercurous chloride | HgCl | 236.06 | .23606 [3] | | |
| Mercury | Hg | 200.6 | .2006 | | |
| Nickel | Ni | 58.68 | .02934 | | |
| Nitric acid | $HNO_3$ | 63.02 | .06302 [2] | | |
| Nitric acid | $HNO_3$ | 63.02 | .021006 [2] | | |
| Nitrogen trioxide | $N_2O_3$ | 76.02 | .019005 [3] | | |
| pentoxide | $N_2O_5$ | 108.02 | .05401 [2] | | |
| pentoxide | $N_2O_5$ | 108.02 | .018033 [3] | | |
| Nitrous acid | $HNO_2$ | 47.02 | .04702 | | |
| Ntirogen | N | 14.008 | .01401 | | |
| Oxalic acid | $H_2C_2O_4$ | 90.03 | .04501 | | |
| Oxalic acid | $H_2C_2O_4 2H_2O$ | 126.06 | .06303 | 4.9° | |
| Phosphoric acid | $H_3PO_4$ | 98.06 | .09806 [2] | v. sol. | M. |
| Phosphoric acid | $H_3PO_4$ | 98.06 | .04903 [2] | v. sol. 0 | P. |
| Phosphoric acid | $H_3PO_4$ | 98.06 | .03268 | v. sol. | |
| Phosphorous acid (ortho) | $H_3PO_3$ | 82.06 | .02735 | | |
| pentoxide | $P_2O_5$ | 142.08 | .02368 | | |
| Potassium | K | 39.10 | .03910 | | |
| bicarbonate | $KHCO_3$ | 100.11 | .10011 | 22.4° | M. |
| bitartrate | $KHC_4H_4O_6$ | 188.16 | .18816 | .37° | P. |
| bromate | $KBrO_3$ | 167.02 | .16702 | | |
| biodate | $KH(IO_3)_2$ | 389.95 | .38995 [2] | | |
| biodate | $KH(IO_3)_2$ | 389.95 | .03249 [3] | | |
| bromide | KBr | 119.02 | .11902 | 53.48° | |
| carbonate | $K_2CO_3$ | 138.20 | .06910 | 89.4° | M. |
| carbonate | $K_2CO_3$ | 138.20 | .06910 [2] | | |
| chlorate | $KClO_3$ | 122.56 | .020427 [3] | 3.3° | |
| Potassium chloride | KCl | 74.56 | .07456 | 28.5° | |
| chromate | $K_2CrO_4$ | 194.20 | .06473 [3] | 61.5° | |
| cyanide | KCN | 65.11 | .06511 [1] | v. sol. | |
| dichromate | $K_2Cr_2O_7$ | 294.20 | .07355 [1] | | |
| dichromate | $K_2Cr_2O_7$ | 294.20 | .14710 [2] | 4.9° | P. |
| dichromate | $K_2Cr_2O_7$ | 294.20 | .04903 [3] | 4.9° | |
| ferrocyanide | $K_4Fe(CN)_6$ | 368.32 | .36832 [3] | | |
| ferrocyanide | $K_4Fe(CN)_6 3H_2O$ | 422.37 | .422.37 [3] | 27.8[12°] | |
| fluoride | KF | 58.10 | .05810 | | |
| hydroxide | KOH | 56.11 | .05611 | 107[15°] | |
| iodate | $KIO_3$ | 214.02 | .03567 | 4.74° | |
| iodide | KI | 166.02 | .16602 | 126.1° | |
| manganate | $K_2MnO_4$ | 197.13 | .049283 [2] | | |
| nitrate | $KNO_3$ | 101.11 | .033703 | 13.3° | |
| nitrite | $KNO_2$ | 85.11 | 08511 | 300[15.5°] | |
| oxalate | $K_2C_2O_4 \cdot H_2O$ | 184.23 | .09211 | | |
| oxide | $K_2O$ | 94.20 | .04710 | v. sol. | |
| perchlorate | $KClO_4$ | 138.56 | .01732 [3] | | |
| permanganate | $KMnO_4$ | 158.03 | .031606 | 2.83° | |
| sulphide | $K_2S$ | 110.26 | .05513 | sol. | |
| sulphocyanate | KCNS | 97.17 | .09717 | 177.2° | |
| tartrate | $K_2C_4H_4O_6$ | 226.25 | .11312 | sol. | |
| Silver | Ag | 107.88 | .10788 | | |

[1] Precipitation reagents. [2] Acids and bases [3] Oxidizing and reducing agents.
M. Methyl orange. P. Phenolphthalein. Temp. C.

## TABLES AND USEFUL DATA

### VII.—USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS (Continued)

| Substance. | Formula. | Molecular or Atomic Weight. | Normal Coefficient 1 c.c. = gm. | Solubility in 100 Gms. Water. | Indicator. |
|---|---|---|---|---|---|
| Silver bromide | AgBr | 187.80 | .18780 | | |
| chloride | AgCl | 143.34 | .14334 | | |
| nitrate | $AgNO_3$ | 169.89 | .16989 | 122° | |
| Sodium | Na | 23.00 | .02300 | | |
| bromide | NaBr | 102.92 | .10292 | 79.5° | |
| bicarbonate | $NaHCO_3$ | 84.01 | .08401 | 6.90° | M. |
| carbonate | $Na_2CO_3$ | 106.005 | .053002 | 7.1° | M. |
| chlorate | $NaClO_3$ | 106.46 | .01774[3] | | |
| chloride | NaCl | 58.46 | .05846 | 35.7° | |
| cyanide | NaCN | 49.01 | .04901 | sol. | |
| hydroxide | NaOH | 40.01 | .04001 | 133.3[18°] | |
| iodide | NaI | 149.92 | .14992 [1] | 158.7° | |
| nitrate | $NaNO_3$ | 85.01 | .02834 | 72.9° | |
| nitrite | $NaNO_2$ | 69.01 | .06901 | 83.3[20°] | |
| oxalate | $Na_2C_2O_4$ | 134.01 | .06700 | 3.22[15.5°] | |
| oxide | $Na_2O$ | 62.00 | .03100 | decomp. | |
| phosphate (mono) | $NaH_2PO_4$ | 120.06 [2] | .12006 | v. sol. | M. |
| phosphate (disod) | $Na_2HPO_4$ | 142.05 [2] | .14205 | ..... | P.orM. |
| phosphate (disod) | $Na_2HPO_412H_2O$ | 358.24 [2] | .35824 | 6.3° | P.orM. |
| phosphate (trisod) | $Na_3PO_4$ | 164.04 [2] | .16404 | ..... | P |
| phosphate | $Na_3PO_4 \cdot 12H_2O$ | 380.24 | .38024[3] | | P |
| sulphide | $Na_2S$ | 78.06 | .03903 | 15.4[10°] | |
| sulphite | $Na_2SO_3$ | 126.06 | .06303 | | |
| thiosulphate | $Na_2S_2O_35H_2O$ | 248.20 | .24820 | 74.7° | |
| thiosulphate | $Na_2S_2O_3 \cdot 5H_2O$ | 248.20 | .24820[3] | | |
| Stannic oxide | $SnO_2$ | 150.70 | .15070 | | |
| Stannous chloride | $SnCl_2$ | 189.62 | .09481 | 83.9° | |
| chloride | $SnCl_22H_2O$ | 225.65 | .112825 | 118.7° | |
| oxide | SnO | 134.70 | .06735 | insol. | |
| Sulphur dioxide | $SO_2$ | 64.06 | .03203 | 7979 cc.[0°] | |
| trioxide | $SO_3$ | 80.06 | .04003 | | |
| Sulphuric acid | $H_2SO_4$ | 98.076 | .049038 | | |
| Sulphurous acid | $H_2SO_3$ | 82.076 | .04104 [2] | | |
| Tartaric acid | $H_2C_4H_4O_6$ | 150.07 | .075035 | 115° | |
| Tin | Sn | 118.70 | .05935 | | |
| Titanium chloride | $TiCl_3$ | 154.48 | .15448 [3] | | |
| Zinc | Zn | 65.37 | .037685 | | |
| carbonate | $ZnCO_3$ | 125.37 | .062685 | .001[15°] | |
| chloride | $ZnCl_2$ | 136.29 | .068145 | 209° | |
| oxide | ZnO | 81.37 | .040685 | .001 | |
| sulphate | $ZnSO_4$ | 161.43 | .080715 | 43.02° | |
| sulphate | $ZnSO_47H_2O$ | 287.54 | .14377 | 115.2° | |
| sulphide | ZnS | 97.43 | .048715 | .00069 | |

[1] Precipitation reagents. [2] Acids and bases. [3] Oxidizing and reducing agents.
M. Methyl orange. P. Phenolphthalein. Temp. C.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS *

| A | B | A′ | B′ | A | B | A′ | B′ |
|---|---|---|---|---|---|---|---|
| Ag | AgBr | 1.7408 | 0.5744 | $AlCl_3$ | Cl | 0.7970 | 1.2547 |
| Ag | AgCl | 1.3287 | 0.7526 | $AlCl_3$ | $H_2SO_4$ | 1.1023 | 0.9072 |
| Ag | AgCN | 1.2411 | 0.8057 | $AlF_3$ | $CaF_2$ | 1.3925 | 0.7182 |
| Ag | AgI | 2.1765 | 0.4595 | $Al_2O_3$ | Al | 0.5303 | 1.8856 |
| Ag | $AgNO_3$ | 1.5748 | 0.6350 | $Al_2O_3$ | $AlCl_3$ | 2.6121 | 0.3828 |
| Ag | $Ag_2O$ | 1.0742 | 0.9310 | $Al_2O_3$ | $Al_2P_2O_7$ | 2.2336 | 0.4482 |
| Ag | $Ag_3PO_4$ | 1.2935 | 0.7731 | $Al_2O_3$ | $Al_2P_2O_5$ | 2.3902 | 0.4184 |
| Ag | $Ag_4P_2O_7$ | 1.4030 | 0.7126 | $Al_2O_3$ | $Al_2(SO_4)_3$ | 3.3504 | 0.2985 |
| Ag | As | 0.2316 | 4.3175 | $Al_2O_3$ | $Al_2(SO_4)_3 \cdot 18H_2O$ | 6.5235 | 0.1533 |
| Ag | Br | 0.7408 | 1.3489 | | | | |
| Ag | HBr | 0.7505 | 1.3324 | $Al_2O_3$ | FeO | 2.1088 | 0.4742 |
| Ag | Cl | 0 3287 | 3.0423 | $Al_2O_3$ | $Fe_2O_3$ | 1.5625 | 0.6400 |
| Ag | HCl | 0.3380 | 2.9590 | $Al_2O_3$ | $H_2SO_4$ | 2.8792 | 0.3473 |
| Ag | HI | 1.1859 | 0.8433 | $Al_2O_3$ | $K_2Al_2(SO_4)_4 \cdot 24H_2O$ | 9.2863 | 0.1077 |
| Ag | I | 1.1765 | 0.8500 | | | | |
| Ag | KBr | 1.1033 | 0.9064 | $Al_2O_3$ | $Na_2Al_2O_4$ | 1.6067 | 0.6224 |
| Ag | KCl | 0.6911 | 1.4469 | $Al_2O_3$ | $(NH_4)_2Al_2(SO_4)_4 \cdot 24H_2O$ | 8.8742 | 0.1127 |
| Ag | $KClO_3$ | 1.1361 | 0.8802 | | | | |
| Ag | $KClO_4$ | 1.2844 | 0.7786 | $Al_2O_3$ | $(SO_3)_3$ | 2.3504 | .04255 |
| Ag | KCN | 0.6035 | 1.6568 | $AlPO_4$ | Al | 0.2219 | 4.5070 |
| Ag | KI | 1 5390 | 0.6498 | $AlPO_4$ | $Al_2O_3$ | 0.4185 | 2.3894 |
| Ag | NaBr | 0 9562 | 1.0458 | $AlPO_4$ | $P_2O_5$ | 0.5815 | 1.7197 |
| Ag | NaCl | 0.5419 | 1.8453 | $Al_2P_2O_7$ | $P_2O_5$ | 0.6224 | 1.6067 |
| Ag | NaI | 1.3897 | 0.7196 | $Al_2P_2O_5$ | $P_2O_5$ | 0.5816 | 1.7193 |
| AgBr | Br | 0.4256 | 2.3498 | $Al_2(SO_4)_3$ | $BaSO_4$ | 1.3635 | 0.7334 |
| AgBr | $BrO_3$ | 0.6811 | 1.4681 | $Al_2(SO_4)_3$ | $H_2SO_4$ | 0.8594 | 1.1636 |
| AgBr | HBr | 0.4311 | 2.3195 | $Al_2(SO_4)_3$ | $NaHCO_3$ | 1.4721 | 0.6793 |
| AgBr | KBr | 0.6337 | 1.5779 | $Al_2(SO_4)_3$ | $SO_3$ | 0.7015 | 1.4255 |
| AgBr | $KBrO_3$ | 0.8893 | 1.1244 | | | | |
| AgBr | NaBr | 0.5480 | 1.8257 | As | Ag | 4.3175 | 0.2316 |
| AgCl | Ag | 0.7526 | 1.3287 | As | $As_2O_3$ | 1.3201 | 0.7575 |
| AgCl | $AgNO_3$ | 1.1852 | 0.8437 | As | $As_2O_5$ | 1.5336 | 0.6521 |
| AgCl | Cl | 0.2474 | 4.0423 | As | $As_2S_3$ | 1.6417 | 0.6091 |
| AgCl | HCl | 0.2545 | 3.9305 | As | 2I | 3.3862 | 0.2953 |
| AgCl | KCl | 0.5202 | 1.9225 | As | $Na_2HAsO_4$ | 2.4809 | 0.4031 |
| AgCl | $KClO_3$ | 0.8550 | 1.1695 | $As_2O_3$ | $As_2O_5$ | 1.1616 | 0.8609 |
| AgCl | NaCl | 0.4078 | 2.4519 | $As_2O_3$ | $As_2S_3$ | 1.2435 | 0.8042 |
| AgCl | $NH_4Cl$ | 0.3732 | 2.6793 | $As_2O_3$ | $As_2S_5$ | 1.5674 | 0.6380 |
| AgCN | KCN | 0.4863 | 2.0564 | $As_2O_3$ | 4I | 2.5652 | 0.3898 |
| AgCN | HCN | 0.2020 | 4.9500 | $As_2O_5$ | $NaH_2AsO_4$ | 1.4264 | 0.7011 |
| AgI | $NH_4I$ | 0.6175 | 1.6194 | $As_2O_5$ | $Na_2HAsO_4$ | 1.6177 | 0.6182 |
| AgI | HI | 0.5448 | 1.8354 | $As_2O_5$ | 4I | 2.2081 | 0.4529 |
| AgI | I | 0.5406 | 1.8500 | | | | |
| AgI | $IO_3$ | 0.7450 | 1.3423 | Au | $AuCl_3$ | 1.5394 | 0.6496 |
| AgI | $I_2O_5$ | 0.8131 | 1.2298 | Au | $HAuCl_4 \cdot 4H_2O$ | 2.0898 | 0.4785 |
| AgI | $I_2O_7$ | 0.7109 | 1.4067 | | | | |
| AgI | KI | 0.7071 | 1.4143 | Au | $KAu(CN)_4 \cdot H_2O$ | 1.8172 | 0.5503 |
| AgI | $KIO_3$ | 0.9115 | 1.0971 | | | | |
| AgI | NaI | 0.6385 | 1.5661 | | | | |
| $AgNO_3$ | $HNO_2$ | 0.3055 | 3.2729 | Ba | $Ba(C_2H_3O_2)_2$ | 1.8594 | 0.5378 |
| $AgNO_3$ | $HNO_3$ | 0.3709 | 2.6959 | Ba | $BaCrO_4$ | 1.8457 | 0.5420 |
| $AgNO_3$ | NaCl | 0.3441 | 2.9061 | Ba | $BaSO_4$ | 1.7010 | 0.5885 |
| $AgNO_3$ | $N_2O_3$ | 0.2470 | 4.0487 | $BaCl_2$ | $BaSO_4$ | 1.1207 | 0.8923 |

$A \times A' = B$ and $B \times B' = A$.

* Compiled and arranged by W. W. Scott and B. S. Clark.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ | A | B | A′ | B′ |
|---|---|---|---|---|---|---|---|
| $BaCl_2$ | $H_2SO_4$ | 0.4709 | 2.1236 | $BaSO_4$ | $SO_3$ | 0.3430 | 2.9155 |
| $BaCO_3$ | $CO_2$ | 0.2229 | 4.4857 | $BaSO_4$ | $SO_4$ | 0.4115 | 2.4301 |
| C(in $BaCO_3$) | $H_2SO_4$ | 8.1740 | 0.1223 | $BaSO_4$ | ZnS | 0.4174 | 2.3957 |
| $BaCrO_4$ | Ba | 0.5420 | 1.8457 | $BaSO_4$ | $ZnSO_4 \cdot 7H_2O$ | 1.2318 | 0.8118 |
| $BaCrO_4$ | $BaSO_4$ | 0.9213 | 1.0854 | | | | |
| $BaCrO_4$ | Cr | 0.2055 | 4.8651 | Be | | See Gl. | |
| $BaCrO_4$ | $Cr_2O_3$ | 0.3002 | 3.3308 | | | | |
| $BaCrO_4$ | $K_2CrO_4$ | 0.7666 | 1.3046 | Bi | $Bi_2O_3$ | 1.1154 | 0.8965 |
| $BaCrO_4$ | $K_2Cr_2O_7$ | 0.5807 | 1.7220 | $BiAsO_4$ | Bi | 0.5994 | 1.6683 |
| $Ba(OH)_2$ | $H_2SO_4$ | 0.5723 | 1.7473 | BiOCl | Bi | 0.8017 | 1.2474 |
| $BaO_2$ | Ba | 0.8208 | 1.2184 | BiOCl | $Bi(NO_3)_3 \cdot 5H_2O$ | 1.8658 | 0.5359 |
| $BaSiF_6$ | Ba | 0.4912 | 2.0359 | | | | |
| $BaSiF_6$ | $BaF_2$ | 0.6271 | 1.5948 | BiOCl | $Bi_2O_3$ | 0.8942 | 1.1184 |
| $BaSiF_6$ | BaO | 0.5484 | 1.8235 | BiOCl | $BiONO_3$ | 1.1024 | 0.9072 |
| $BaSiF_6$ | F | 0.4076 | 2.4533 | $Bi_2O_3$ | Bi | 0.8965 | 1.1154 |
| $BaSiF_6$ | HF | 0.4292 | 2.3297 | $Bi_2O_3$ | $BiONO_3$ | 1.2328 | 0.8112 |
| $BaSiF_6$ | $H_2SiF_6$ | 0.5160 | 1.9379 | $Bi_2O_3$ | $Bi(NO_3)_3 \cdot 5H_2O$ | 2.0867 | 0.4792 |
| $BaSiF_6$ | $SiF_4$ | 0.3729 | 2.6814 | | | | |
| $BaSiF_6$ | $SiO_2$ | 0.2156 | 4.6380 | $Bi_2S_3$ | Bi | 0.8122 | 1.2313 |
| $BaSO_4$ | $Al_2(SO_4)_3$ | 0.7334 | 1.3635 | $Bi_2S_3$ | $Bi_2O_3$ | 0.9059 | 1.1039 |
| $BaSO_4$ | Ba | 0.5885 | 1.7010 | | | | |
| $BaSO_4$ | $BaCl_2$ | 0.8928 | 1.1207 | B | $KBF_4$ | 11.464 | 0.0872 |
| $BaSO_4$ | $BaCl_2 \cdot 2H_2O$ | 1.0466 | 0.9554 | $B_2O_3$ | B | 0.3143 | 3.1819 |
| $BaSO_4$ | $BaCO_3$ | 0.8455 | 1.1827 | $B_2O_3$ | $KBF_4$ | 3.6029 | 0.2775 |
| $BaSO_4$ | $BaCrO_4$ | 1.0854 | 0.9213 | $B_2O_3$ | $H_3BO_3$ | 1.7721 | 0.5643 |
| $BaSO_4$ | $Ba(NO_3)_2$ | 1.1197 | 0.8931 | $B_2O_3$ | $Na_2B_4O_7 \cdot 10H_2O$ | 5.4594 | 0.1832 |
| $BaSO_4$ | BaO | 0.6571 | 1.5219 | | | | |
| $BaSO_4$ | $BaO_2$ | 0.7256 | 1.3782 | $KBF_4$ | $H_3BO_3$ | 0.4919 | 2.0331 |
| $BaSO_4$ | $Ba_3(PO_4)_2$ | 0.8456 | 1.1826 | $KBF_4$ | $Na_2B_4O_7 \cdot 10H_2O$ | 0.7576 | 1.3199 |
| $BaSO_4$ | BaS | 0 7258 | 1.3778 | | | | |
| $BaSO_4$ | $CaSO_3$ | 0.5147 | 1.9429 | | | | |
| $BaSO_4$ | $CaSO_4$ | 0.5832 | 1.7147 | Br | Ag | 1.3498 | 0.7408 |
| $BaSO_4$ | FeS | 0.3766 | 2.6554 | Br | AgBr | 2.3498 | 0.4256 |
| $BaSO_4$ | $H_2S$ | 0.1460 | 6.8493 | Br | HBr | 1.0130 | 0.9877 |
| $BaSO_4$ | $H_2SO_3$ | 0.3517 | 2.8437 | Br | O | 0.1001 | 9.9913 |
| $BaSO_4$ | $H_2SO_4$ | 0.4202 | 2.3801 | $BrO_3$ | Ag | 0.8433 | 1.1858 |
| $BaSO_4$ | $K_2Al_2(SO_4)_4 \cdot 24H_2O$ | 1 0167 | 0.9839 | $BrO_3$ | AgBr | 1.4681 | 0.6811 |
| $BaSO_4$ | $KHSO_4$ | 0.5834 | 1.7141 | | | | |
| $BaSO_4$ | MgO | 0.1727 | 5.7897 | Ca | $CaCl_2$ | 2.7687 | 0.3612 |
| $BaSO_4$ | $MgSO_4 \cdot 7H_2O$ | 1.0560 | 0.9469 | Ca | CaO | 1.3993 | 0.7146 |
| $BaSO_4$ | $MnSO_4$ | 0.6469 | 1.5458 | Ca | $Cl_2$ | 1.7690 | 0.5653 |
| $BaSO_4$ | $Na_2CO_3$ | 0.4541 | 2.2022 | $Ca(CH_3CO_2)_2$ | CaO | 0.3546 | 2.8200 |
| $BaSO_4$ | $NaHSO_3$ | 0.4458 | 2.2432 | $Ca(CH_3CO_2)_2$ | $CH_3CO_2H$ | 0.7594 | 1.3169 |
| $BaSO_4$ | $Na_2O$ | 0.2656 | 3.7651 | $Ca(CH_3CO_2)_2$ | $H_2SO_4$ | 0.6203 | 1.6120 |
| $BaSO_4$ | $Na_2S$ | 0.3344 | 2.9904 | $CaCl_2$ | $CaCO_3$ | 0.9016 | 1.1091 |
| $BaSO_4$ | $Na_2SO_3$ | 0.5401 | 1.8515 | $CaCl_2$ | CaO | 0.5052 | 1.9795 |
| $BaSO_4$ | $Na_2S_2O_3$ | 0.3387 | 2.9524 | $CaCl_2$ | $CaSO_4$ | 1.2265 | 0.8153 |
| $BaSO_4$ | $Na_2SO_4$ | 0.6086 | 1.6431 | $CaCl_2$ | $Cl_2$ | 0.6390 | 1.5650 |
| $BaSO_4$ | $Na_2SO_4 \cdot 10H_2O$ | 1.3804 | 0.7244 | $CaCO_3$ | Ca | 0.4006 | 2.4966 |
| | | | | $CaCO_3$ | $CaCl_2$ | 1.1091 | 0.9016 |
| $BaSO_4$ | $NH_4)_2SO_4$ | 0.5661 | 1.7665 | $CaCO_3$ | $Ca(HCO_3)_2$ | 1.6197 | 0.6174 |
| $BaSO_4$ | $PbSO_4$ | 1.2987 | 0.7700 | $CaCO_3$ | CaO | 0.5603 | 1.7847 |
| $BaSO_4$ | S | 0.1373 | 7.2812 | $CaCO_3$ | $CO_2$ | 0.4397 | 2.2743 |
| $BaSO_4$ | $SO_2$ | 0.2744 | 3.6443 | $CaCO_3$ | $CaSO_4$ | 1.3604 | 0.7351 |
| | | | | $CaCO_3$ | $CaSO_4 \cdot 2H_2O$ | 1.7204 | 0.5813 |

A×A′=B and B×B′=A.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ | A | B | A′ | B′ |
|---|---|---|---|---|---|---|---|
| $CaCO_3$ | $Na_2CO_3$ | 1.0593 | 0.9441 | $CaSO_4$ | $CaCl_2$ | 0.8153 | 1.2265 |
| $CaCO_3$ | HCl | 0.7288 | 1.3720 | $CaSO_4$ | $CaF_2$ | 0.5735 | 1.7438 |
| $CaF_2$ | $AlF_3$ | 0.7182 | 1.3925 | $CaSO_4$ | CaO | 0.4119 | 2.4280 |
| $CaF_2$ | Ca | 0.5128 | 1.9501 | $CaSO_4$ | F | 0.2791 | 3.5827 |
| $CaF_2$ | $CaSO_4$ | 1.7438 | 0.5735 | $CaSO_4$ | HF | 0.2539 | 3.4021 |
| $CaF_2$ | F | 0.4867 | 2.0545 | $CaSO_4$ | $H_2SO_4$ | 0.7205 | 1.3875 |
| $CaF_2$ | HF | 0.5126 | 1.9508 | $CaSO_4$ | $SO_3$ | 0.5881 | 1.7003 |
| $CaF_2$ | $H_2SiF_6$ | 1.8485 | 0.5410 | $CaSO_4 \cdot 2H_2O$ | CaO | 0.3257 | 3.0707 |
| $CaF_2$ | NaF | 1.0760 | 0.9294 | | | | |
| $Ca(HCO_3)_2$ | CaO | 0.3459 | 2.8908 | Cb | $Cb_2O_5$ | 1.4278 | 0.7004 |
| $Ca(HCO_3)_2$ | $CO_2$ | 0.5429 | 1.8419 | | | | |
| $CaHPO_4$ | CaO | 0.4119 | 2.4276 | Cd | CdO | 1.1426 | 0.8754 |
| $CaHPO_4$ | $Ca_2P_2O_7$ | 0.9338 | 1.0709 | Cd | CdS | 1.2853 | 0.7780 |
| $CaHPO_4$ | $P_2O_5$ | 0.5219 | 1.9161 | Cd | $CdSO_4$ | 1.8547 | 0.5392 |
| $Ca(H_2PO_4)_2$ | $NaHCO_3$ | 0.7175 | 1.3938 | Cd | S | 0.2853 | 3.5048 |
| $Ca(H_2PO_4)_2$ | $P_2O_5$ | 0.6067 | 1.6483 | CdO | CdS | 1.1251 | 0.8888 |
| $CaH_2P_2O_7$ | $Ca(H_2PO_4)_2$ | 1.0827 | 0.9236 | CdS | $H_2S$ | 0.2327 | 4.2975 |
| $CaH_2P_2O_7$ | CaO | 0.2594 | 3.8553 | CdS | S | 0.2220 | 4.5048 |
| $CaH_2P_2O_7$* | $NaHCO_3$ | 0.7773 | 1.2866 | | | | |
| $CaH_2P_2O_7$ | $P_2O_5$ | 0.6573 | 1.5214 | Ce | $Ce(NO_3)_4$ | 2.7685 | 0.3612 |
| $Ca(HSO_3)_2$ | CaO | 0.2773 | 3.6067 | Ce | $Ce_2O_3$ | 1.1711 | 0.8539 |
| $Ca(HSO_3)_2$ | $SO_2$ | 0.6336 | 1.5783 | Ce | $CeO_2$ | 1.2282 | 0.8142 |
| $Ca(NO_3)_2$ | $N_2O_5$ | 0.6582 | 1.5192 | Ce | $Ce(SO_4)_3$ | 2.0275 | 0.4932 |
| CaO | Ca | 0.7146 | 1.3993 | $Ce_2O_3$ | $CeO_2$ | 1.0487 | 0.9536 |
| CaO | $Ca(CH_3CO_2)_2$ | 2.8200 | 0.3546 | | | | |
| CaO | $CaCl_2$ | 1.9795 | 0.5052 | $CH_2ClCO_2H$ | Cl | 0.3753 | 2.6645 |
| CaO | $CaCO_3$ | 1.7847 | 0.5603 | $CH_3CHOH$ $CO_2H$ | $H_2SO_4$ | 0.5446 | 1.8361 |
| CaO | $CaF_2$ | 1.3924 | 0.7182 | | | | |
| CaO | $Ca(HCO_3)_2$ | 2.8908 | 0.3459 | $CH_3CO_2H$ | $Ca(CH_3CO_2)_2$ | 1.3169 | 0.7594 |
| CaO | $Ca(H_2PO_4)_2$ | 4.1766 | 0.2394 | $CH_3CO_2H$ | $CH_3CO_2Na$ | 1.3663 | 0.7319 |
| CaO | $CaH_2P_2O_7$ | 3.8553 | 0.2594 | $CH_3CO_2H$ | $(CH_3CO)_2O$ | 0.8499 | 1.1766 |
| CaO | $Ca(HSO_3)_2$ | 3.6067 | 0.2773 | $CN_3CO_2H$ | $H_2SO_4$ | 0.8169 | 1.2241 |
| CaO | $Ca_3P_2O_8$ | 1.8446 | 0.5421 | $CH_3CO_2H$ | $Na_2CO_3$ | 0.8828 | 1.1327 |
| CaO | $CaSO_3$ | 2.1427 | 0.4667 | $CH_3CO_2H$ | $Na_2O$ | 0.5164 | 1.9365 |
| CaO | $CaSO_4$ | 2.4280 | 0.4119 | $CH_3CO_2H$ | Pb | 1.7249 | 0.5797 |
| CaO | $CaSO_4 \cdot 2H_2O$ | 3.0707 | 0.3257 | $CH_3CO_2Na$ | $H_2SO_4$ | 0.5979 | 1.6725 |
| CaO | $CH_3CO_2H$ | 2.1413 | 0.4670 | $CH_3CO_2Na$ | $Na_2O$ | 0.3779 | 2.6459 |
| CaO | $CO_2$ | 0.7874 | 1.2743 | $CH_3CO_2Na$ | $Na_2SO_4$ | 0.8660 | 1.1547 |
| CaO | $H_2SO_4$ | 1.7494 | 0.5716 | $(CH_3CO)_2O$ | $H_2SO_4$ | 0.9612 | 1.0404 |
| CaO | NaCl | 2.0852 | 0.4786 | $C_6H_2O_4$ | $H_2SO_4$ | 1.0897 | 0.9177 |
| CaO | $Na_2CO_3$ | 1.8905 | 0.5290 | $C_2H_2O_4 \cdot 2H_2O$ | $H_2SO_4$ | 0.7782 | 1.2851 |
| CaO | $Na_2SO_4$ | 2.5338 | 0.3947 | $C_4H_6O_6$ | $H_2SO_4$ | 0.6537 | 1.5298 |
| CaO | S | 0.5720 | 1.7484 | $C_4H_6O_6$ | $NaHCO_3$ | 1.1197 | 0.8931 |
| CaO | $SO_3$ | 1.4280 | 0.7003 | $C_4H_4O_6HK$ | $H_2SO_4$ | 0.2607 | 3.8362 |
| $Ca_3P_2O_8$ | CaO | 0.5421 | 1.8446 | | | | |
| $Ca_3P_2O_8$ | $Mg_2P_2O_7$ | 0.7178 | 1.3932 | Cl | Ag | 3.0423 | 0.3287 |
| $Ca_3P_2O_8$ | $(NH_4)_3PO_4 \cdot 12MoO_3$ | 12.102 | 0.0826 | Cl | AgCl | 4.0423 | 0.2474 |
| | | | | Cl | $AgNO_3$ | 4.7910 | 0.2088 |
| $Ca_3P_2O_8$ | $P_2O_5$ | 0.4579 | 2.1839 | Cl | $AlCl_3$ | 1.2547 | 0.7970 |
| CaS | $BaSO_4$ | 3.2347 | 0.3091 | Cl | $BaCrO_4$ | 3.5741 | 0.2798 |
| $CaSO_3$ | $BaSO_4$ | 1.9429 | 0.5147 | Cl | $CH_2ClCO_2H$ | 2.6645 | 0.3753 |
| $CaSO_3$ | CaO | 0.4667 | 2.1427 | Cl | Ca | 0.5653 | 1.7690 |
| $CaSO_4$ | $BaSO_4$ | 1.7147 | 0.5832 | Cl | $CaCl_2$ | 1.5650 | 0.6390 |

$A \times A' = B$ and $B \times B' = A$.

* Phenolphthalein indicator.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ |
|---|---|---|---|
| Cl | CsCl | 4.7454 | 0.2107 |
| Cl | HCl | 1.0284 | 0.9724 |
| Cl | $H_2SO_4$ | 1.3831 | 0.7230 |
| Cl | I | 3.5792 | 0.2794 |
| Cl | K | 1.1027 | 0.9069 |
| Cl | KCl | 2.1027 | 0.4756 |
| Cl | $KClO_3$ | 3.4563 | 0.5386 |
| Cl | $KClO_4$ | 3.9075 | 0.5919 |
| Cl | Li | 0.1974 | 5.0657 |
| Cl | Mg | 0.3429 | 2.9162 |
| Cl | $MgCl_2$ | 1.3429 | 0.7447 |
| Cl | $MgCl_2 \cdot 6H_2O$ | 2.8672 | 0.3488 |
| Cl | MgO in $MgCl_2$ | 0.5685 | 1.7590 |
| Cl | $MnO_2$ | 1.2257 | 0.8158 |
| Cl | Na | 0.6486 | 1.5417 |
| Cl | NaCl | 1.6486 | 0.6066 |
| Cl | $NaClO_3$ | 3.0023 | 0.3331 |
| Cl | $NaClO_4$ | 3.4535 | 0.2896 |
| Cl | $NH_4$ | 0.5088 | 1.9656 |
| Cl | $NH_4Cl$ | 1.5088 | 0.6628 |
| Cl | Rb | 2.4098 | 0.4150 |
| Cl | RbCl | 3.4098 | 0.2933 |
| Cl | Sn in $SnCl_4$ | 0.8390 | 1.1919 |
| Cl | $SnCl_4$ | 1.8390 | 0.5438 |
| Cl | $PbCl_2$ | 3.9202 | 0.2551 |
| Cl | $PbCrO_4$ | 4.5572 | 0.2194 |
| Cl | $ZnCl_2$ | 1.9217 | 0.5204 |
| Co | $CoNO_3 \cdot 6H_2O$ | 4.9361 | 0.2026 |
| Co | $Co(NO_2)_3(KNO_2)_3$ | 7.6706 | 0.1304 |
| Co | CoO | 1.2714 | 0.7866 |
| Co | $Co_3O_4$ | 1.3053 | 0.7661 |
| Co | $CoSO_4 \cdot 7H_2O$ | 4.7677 | 0.2097 |
| CoO | $Co_3O_4$ | 2.0680 | 0.9336 |
| $CO_2$ | $BaCO_3$ | 4.4857 | 0.2229 |
| $CO_2$ | BaO | 3.4857 | 0.2869 |
| $CO_2$ | $Ba(HCO_3)_2$ | 2.9476 | 0.3393 |
| $CO_2$ | C | 0.2727 | 3.6667 |
| $CO_2$ | $CaCO_3$ | 2.2743 | 0.4397 |
| $CO_2$ | $Ca(HCO_3)_2$ | 1.8419 | 0.5429 |
| $CO_2$ | CaO | 1.2743 | 0.7847 |
| $CO_2$ | $CO_3$ | 1.3636 | 0.7333 |
| $CO_2$ | $CsCO_3$ | 7.4005 | 0.1351 |
| $CO_2$ | $FeCO_3$ | 2.6327 | 0.3798 |
| $CO_2$ | $Fe(HCO_3)_2$ | 2.0211 | 0.4948 |
| $CO_2$ | $H_2SO_4$ | 2.2292 | 0.4486 |
| $CO_2$ | $K_2CO_3$ | 3.1409 | 0.3184 |
| $CO_2$ | $K_2O$ | 2.1409 | 0.4671 |
| $CO_2$ | $LiCO_3$ | 1.6818 | 0.5946 |
| $CO_2$ | $LiHCO_3$ | 1.5457 | 0.6470 |
| $CO_2$ | $Li_2O$ | 0.6818 | 1.4667 |
| $CO_2$ | $MgCO_3$ | 1.9164 | 0.5218 |
| $CO_2$ | $Mg(HCO_3)_2$ | 1.6629 | 0.6013 |
| $CO_2$ | MgO | 0.9164 | 1.0913 |
| $CO_2$ | $MnCO_3$ | 2.6121 | 0.3828 |
| $CO_2$ | $Mn(HCO_3)_2$ | 2.0108 | 0.4973 |
| $CO_2$ | MnO | 1.6121 | 0.6203 |
| $CO_2$ | $Na_2CO_3$ | 2.4091 | 0.4151 |
| $CO_2$ | $NaHCO_3$ | 1.9093 | 0.5238 |
| $CO_2$ | $Na_2SO_4$ | 3.6667 | 0.2727 |
| $CO_2$ | $Na_2O$ | 1.4091 | 0.7097 |
| $CO_2$ | $(NH_4)_2CO_3$ | 2.1836 | 0.4579 |
| $CO_2$ | $PbCO_3$ | 6.0705 | 0.1647 |
| $CO_2$ | $Rb_2CO_3$ | 5.2477 | 0.1906 |
| $CO_2$ | $RbHCO_3$ | 3.3273 | 0.3006 |
| $CO_2$ | $Rb_2O$ | 4.2478 | 0.2354 |
| $CO_2$ | $SrCO_3$ | 3.3551 | 0.2981 |
| $CO_2$ | $Sr(HCO_3)_2$ | 2.3823 | 0.4198 |
| $CO_2$ | SrO | 2.3550 | 0.4246 |
| $CO_2$ | $ZnCO_3$ | 2.8493 | 0.3510 |
| Cr | $BaCrO_4$ | 4.8651 | 0.2055 |
| Cr | $Cr_2O_3$ | 1.4606 | 0.6846 |
| Cr | $PbCrO_4$ | 6.2136 | 0.1609 |
| Cr | $K_2Cr_2O_7$ | 2.8029 | 0.3535 |
| $Cr_2O$ | $BaCrO_4$ | 3.3308 | 0.3002 |
| $Cr_2O$ | $CrO_3$ | 1.3157 | 0.7602 |
| $Cr_2O$ | $PbCrO_4$ | 4.2513 | 0.2352 |
| $CrO_3$ | $BaCrO_4$ | 2.5322 | 0.3949 |
| $CrO_3$ | $K_2CrO_4$ | 1.9411 | 0.5152 |
| $CrO_3$ | $K_2Cr_2O_7$ | 1.4706 | 0.6800 |
| $CrO_3$ | $PbCrO_4$ | 3.2233 | 0.3097 |
| Cs | CsCl | 1.2670 | 0.7893 |
| Cs | $Cs_2O$ | 1.0602 | 0.9432 |
| Cs | $Cs_2CO_3$ | 1.2258 | 0.8157 |
| Cs | $Cs_2SO_4$ | 1.3617 | 0.7344 |
| $CsPtCl_6$ | Cs | 0.3945 | 2.5351 |
| $CsPtCl_6$ | $Cs_2O$ | 0.4182 | 2.3911 |
| Cu | CuO | 1.2517 | 0.7989 |
| Cu | $Cu_2O$ | 1.1258 | 0.8888 |
| Cu | $Cu_2S$ | 1.2522 | 0.7986 |
| Cu | $CuSO_4$ | 2.5112 | 0.3982 |
| Cu | $CuSO_4 \cdot 5H_2O$ | 3.9283 | 0.2546 |
| CuCNS | Cu | 0.5226 | 1.9137 |
| CuCNS | CuO | 0.6541 | 1.5288 |
| CuO | $CuSO_4$ | 2.0062 | 0.4985 |
| CuO | $H_2SO_4$ | 1.2327 | 0.8112 |
| CuO | $CuSO_4 \cdot 5H_2O$ | 3.1383 | 0.3186 |
| CuS | S | 0.3353 | 2.9822 |
| $Cu_2S$ | CuO | 0.9996 | 1.0004 |
| $Cu_2S$ | $Cu_2O$ | 0.8991 | 1.1122 |
| $Er_2O_3$ | Er | 0.8746 | 1.1433 |
| F | $BaSiF_6$ | 2.4533 | 0.4076 |

$A \times A' = B$ and $B \times B' = A$.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ | A | B | A′ | B′ |
|---|---|---|---|---|---|---|---|
| F | $CaF_2$ | 2.0545 | 0.4868 | $FeS_2$ | S | 0.5346 | 1.8706 |
| F | $CaSO_4$ | 3.5827 | 0.2791 | $FeSO_4$ | $H_2SO_4$ | 0.6457 | 1.5487 |
| F | HF | 1.0531 | 0.9496 | $FeSO_4 \cdot 7H_2O$ | $H_2SO_4$ | 0.3528 | 2.8345 |
| F | $H_2SiF_6$ | 1.2660 | 0.7899 | $Fe_2(SO_4)_3$ | $H_2SO_4$ | 0.7358 | 1.3590 |
| F | $K_2SiF_6$ | 1.9342 | 0.5170 | $FeSO_4(NH_4)_2$ $SO_4 \cdot 6H_2O$ | $Na_2Cr_2O_7$ | 0.1114 | 8.9808 |
| F | NaF | 2.2105 | 0.4524 | | | | |
| Fe | $FeCl_2$ | 2.2701 | 0.4405 | $Ga_2O_3$ | Ga | 0.7444 | 1.3434 |
| Fe | $FeCl_3 \cdot 6H_2O$ | 4.8410 | 0.2066 | $Ga_2S_3$ | Ga | 0.5923 | 1.6882 |
| Fe | $Fe(HCO_3)_2$ | 3.1851 | 0.3140 | | | | |
| Fe | FeO | 1.2865 | 0.7773 | $GeO_2$ | Ge | 0.6938 | 1.4414 |
| Fe | $Fe_2O_3$ | 1.4298 | 0.6994 | $K_2GeF_6$ | Ge | 0.2739 | 3.6510 |
| Fe | $Fe_3O_4$ | 1.3820 | 0.7236 | | | | |
| Fe | $FePO_4$ | 2.7020 | 0.3701 | GlO | Gl | 0.3626 | 2.7582 |
| Fe | FeS | 1.5743 | 0.6352 | GlO | $GlCl_2$ | 3.1881 | 0.3137 |
| Fe | $FeSO_4$ | 2.7205 | 0.3676 | GlO | $GlSO_4 \cdot 4H_2O$ | 7.0607 | 0.1416 |
| Fe | $FeSO_4 \cdot 7H_2O$ | 4.9789 | 0.2008 | | | | |
| Fe | $Fe_2(SO_4)_3$ | 3.5807 | 0.2793 | H | $H_2O$ | 8.9363 | 0.1119 |
| Fe | $FeSO_4(NH_4)_2$ $SO_4$ | 7.0225 | 0.1424 | $H_3BO_3$ | $B_2O_3$ | 0.5643 | 1.7721 |
| Fe (titr. equiv.) | $HNO_3$ | 0.5643 | 1.7721 | HBr | Ag | 1.3324 | 0.7505 |
| Fe | $Na_2Cr_2O_7$ | 0.7820 | 1.2788 | HBr | AgBr | 2.3195 | 0.4311 |
| $FeCO_3$ | $CO_2$ | 0.3798 | 2.6327 | HCl | AgCl | 3.9305 | 0.2544 |
| $Fe(HCO_3)_2$ | $CO_2$ | 0.4948 | 2.0211 | HCl | $CaCO_3$ | 1.3720 | 0.7288 |
| FeO | $Al_2O_3$ | 0.4742 | 2.1088 | HCl | Cl | 0.9724 | 1.0284 |
| FeO | $FeCO_3$ | 1.6125 | 0.6202 | HCl | $HNO_2$ | 1.2893 | 0.7756 |
| FeO | $Fe(HCO_3)_2$ | 2.4757 | 0.4039 | HCl | $HNO_3$ | 1.7280 | 0.5787 |
| FeO | $Fe_2O_3$ | 1.1114 | 0.8998 | HCl | $H_2SO_3$ | 1.1255 | 0.8885 |
| FeO | $FePO_4$ | 2.1002 | 0.4761 | HCl | $H_2SO_4$ | 1.3448 | 0.7436 |
| FeO | FeS | 1.2237 | 0.8172 | HCl | KCl | 2.0445 | 0.4891 |
| FeO | $FeSO_4$ | 2.1146 | 0.4729 | HCl | $K_2O$ | 1.2915 | 0.7743 |
| FeO | $FeSO_4 \cdot 7H_2O$ | 3.8700 | 0.2584 | HCl | NaCl | 1.6030 | 0.6239 |
| FeO | $H_2SO_4$ | 1.3653 | 0.7324 | HCl | $Na_2CO_3$ | 1.4533 | 0.6881 |
| FeO | $SO_3$ | 1.1146 | 0.8972 | HCl | $NH_4Cl$ | 1.4669 | 0.6817 |
| $Fe_2O_3$ | $Al_2O_3$ | 0.6400 | 1.5625 | HCl | $SnCl_4$ | 1.7882 | 0.5592 |
| $Fe_2O_3$ | $FeCl_3$ | 2.0318 | 0.4922 | | | | |
| $Fe_2O_3$ | $FeCO_3$ | 1.4509 | 0.6892 | $HCO_2H$ | $H_2SO_4$ | 1.0658 | 0.9383 |
| $Fe_2O_3$ | $Fe(HCO_3)_2$ | 2.2277 | 0.4489 | | | | |
| $Fe_2O_3$ | $Fe_3O_4$ | 0.9666 | 1.0346 | HF | $BaSiF_6$ | 2.3297 | 0.4292 |
| $Fe_2O_3$ | $FePO_4$ | 1.8898 | 0.5292 | HF | $CaF_2$ | 1.9508 | 0.5126 |
| $Fe_2O_3$ | FeS | 1.1011 | 0.9082 | HF | $CaSO_4$ | 3.4021 | 0.2939 |
| $Fe_2O_3$ | $FeS_2$ | 1.5028 | 0.6655 | HF | F | 0.9496 | 1.0531 |
| $Fe_2O_3$ | $FeSO_4$ | 1.9027 | 0.5256 | HF | $H_2SO_4$ | 2.4510 | 0.4080 |
| $Fe_2O_3$ | $FeSO_4 \cdot 7H_2O$ | 3.4822 | 0.2872 | HF | $K_2SiF_6$ | 1.8368 | 0.5444 |
| $Fe_2O_3$ | $FeSO_4(NH_4)_2$ $SO_4 \cdot 6H_2O$ | 4.9118 | 0.2036 | HF(2HF) | $H_2SiF_6$ | 3.6065 | 0.2773 |
| | | | | HF(6HF) | $H_2SiF_6$ | 1.2022 | 0.8318 |
| $Fe_2O_3$ | $Fe_2(SO_4)_3$ | 2.5032 | 0.3993 | | | | |
| $Fe_2O_3$ | $H_2SO_4$ | 1.8428 | 0.5427 | Hg | HgCl | 1.1768 | 0.8498 |
| $Fe_2O_3$ | $SO_3$ | 1.5032 | 0.6648 | Hg | $HgCl_2$ | 1.3535 | 0.7388 |
| $FePO_4$ | $P_2O_5$ | 0.4708 | 2.1239 | Hg | HgO | 1.0798 | 0.9261 |
| FeS | $BaSO_4$ | 2.6554 | 0.3766 | Hg | HgS | 1.1599 | 0.8622 |
| FeS | $H_2S$ | 0.3877 | 2.5791 | HgCl | $SnCl_2$ | 0.4023 | 2.4859 |
| FeS | $H_2SO_4$ | 1.1155 | 0.9863 | HgCl | $SnCl_4$ | 0.5525 | 1.8100 |
| FeS | S | 0.3648 | 2.7431 | $HgCl_2$ | HgCl | 0.8694 | 1.1502 |
| $FeS_2$ | $Fe_2O_3$ | 0.6654 | 1.5029 | $HgCl_2$ | HgS | 0.8569 | 1.1670 |

A×A′=B and B×B′=A.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ |
|---|---|---|---|
| HgO | HgCl | 1.1827 | 0.8455 |
| $Hg_2O$ | HgCl | 1.1321 | 0.8834 |
| HgS | $Hg(CN)_2$ | 1.0860 | 0.9208 |
| HgS | $HgNO_3$ | 1.1290 | 0.8857 |
| HgS | $Hg(NO_3)_2$ | 1.3962 | 0.7162 |
| HgS | $Hg_2O$ | 0.8963 | 1.1158 |
| HgS | HgO | 0.9307 | 1.0744 |
| HgS | $HgSO_4$ | 1.2758 | 0.7838 |
| HI | A | 0.8433 | 1.1859 |
| HI | AgI | 1.8354 | 0.5448 |
| HI | Pd | 0.4170 | 2.3979 |
| HI | $PdI_2$ | 1.4092 | 0.7097 |
| HI | Tl | 2.5868 | 0.3866 |
| $HNO_2$ | $AgNO_2$ | 3.2729 | 0.3055 |
| $HNO_2$ | HCl | 0.7756 | 1.2893 |
| $HNO_2$ | $H_2SO_4$ | 1.0431 | 0.9587 |
| $HNO_2$ | NO | 0.6382 | 1.5667 |
| $HNO_3$ | Cl | .5627 | 1.7772 |
| $HNO_3$ | HCl | 0.5787 | 1.7280 |
| $HNO_3$ | $H_2SO_4$ | 0.7782 | 1.2850 |
| $HNO_3$ | $KNO_3$ | 1.6045 | 0.6233 |
| $HNO_3$ | N | 0.2223 | 4.4981 |
| $HNO_3$ | $NaNO_3$ | 1.3490 | 0.7413 |
| $HNO_3$ | $NH_3$ | 0.2702 | 3.7006 |
| $HNO_3$ | $NH_4Cl$ | 0.8489 | 1.1780 |
| $HNO_3$ | $(NH_4)_2PtCl_6$ | 3.5215 | 0.2840 |
| $HNO_3$ | NO | 0.4 62 | 2.0999 |
| $HNO_3$ | $N_2O_3$ | 0.6032 | 1.6579 |
| $HNO_3$ | $N_2O_4$ | 0.7301 | 1.3697 |
| $HNO_3$ | $N_2O_5$ | 0.8571 | 1.1668 |
| $HNO_3$ | Pt | 1.5471 | 0.6464 |
| $H_3PO_4$ | $HPO_3$ | 0.8163 | 1.2251 |
| $H_3PO_4$ | $H_4P_2O_7$ | 0.9081 | 1.1012 |
| $H_3PO_4$ | $H_2SO_4$ | 1.0002 | 0 9998 |
| $H_3PO_4$ | $Mg_2P_2O_7$ | 1.1356 | 0.8806 |
| $H_3PO_4$ | P | 0.3165 | 3.1593 |
| $H_3PO_4$ | $P_2O_5$ | 0.7244 | 1.3804 |
| $H_2PtCl_6 \cdot 6H_2O$ | Pt | 0.376 | 2.6558 |
| $H_2S$ | $As_2S_3$ | 2.4074 | 0.4154 |
| $H_2S$ | $BaSO_4$ | 6.8493 | 0.1460 |
| $H_2S$ | CdS | 4.2379 | 0.2360 |
| $H_2S$ | FeS | 2.5791 | 0.3877 |
| $H_2S$* | $H_2SO_4$ | 1.4388 | 0.6950 |
| $H_2S$ | S | 0.9388 | 1.0629 |
| $H_2S$ | $SO_2$ | 1.8835 | 0.5309 |
| $H_2S$ | $SO_3$ | 2.3488 | 0.4258 |
| $H_2SeO_3$ | Se | 0.6129 | 1.6315 |
| $H_2SiF_6$ | $BaSiF_6$ | 1.9379 | 0.5160 |
| $H_2SiF_6$ | $CaF_2$ | 0.54 0 | 1.8485 |
| $H_2SiF_6$ | F | 0.7899 | 1.2660 |
| $H_2SiF_6$ | 2HF | 0.2773 | 3.6065 |
| $H_2SiF_6$ | 6HF | 0.8318 | 1.2022 |
| $H_2SiF_6$ | $H_2SO_4$ | 2.0391 | 0.4904 |
| $H_2SiF_6$ | $K_2SiF_6$ | 1.5279 | 0.6545 |
| $H_2SiF_6$ | $SiF_4$ | 0.7227 | 1.3837 |
| $H_2SiF_6$ | $SiF_6$ | 0.9860 | 1.0141 |
| $H_2SiO_3$ | $SiO_2$ | 0.7699 | 1.2988 |
| $H_2SO_3$ | $BaSO_4$ | 2.8437 | 0.3517 |
| $H_2SO_3$ | HCl | 0.8885 | 1.1255 |
| $H_2SO_3$ | $H_2SO_4$ | 1.1949 | 0.8369 |
| $H_2SO_3$ | $SO_2$ | 0.7805 | 1.2812 |
| $H_2SO_4$ | $AlCl_3$ | 0.9072 | 1.1023 |
| $H_2SO_4$ | $Al_2O_3$ | 0.3473 | 2.8792 |
| $H_2SO_4$ | $Al_2(SO_4)_3$ | 1.1636 | 0.8594 |
| $H_2SO_4$ | $Ba(OH)_2$ | 1.7473 | 0.5723 |
| $H_2SO_4$ | $BaSO_4$ | 2.3800 | 0.4202 |
| $H_2SO_4$ | C(in $BaCO_3$) | 0.1223 | 8.1740 |
| $H_2SO_4$ | $Ca(CH_3CO_2)_2$ | 1.6120 | 0.6203 |
| $H_2SO_4$ | CaO | 0.5716 | 1.7494 |
| $H_2SO_4$ | $CaSO_4$ | 1.3878 | 0.7205 |
| $H_2SO_4$ | $CH_3CHOH$ $CO_2H$ | 1.8361 | 0.5446 |
| $H_2SO_4$ | $CH_3CO_2H$ | 1.2241 | 0.8169 |
| $H_2SO_4$ | $CH_3CO_2Na$ | 1.6725 | 0.5979 |
| $H_2SO_4$ | $(CH_3CO_2)_2O$ | 1.0404 | 0.9612 |
| $H_2SO_4$ | $C_2H_2O_4$ | 0.9177 | 1.0897 |
| $H_2SO_4$ | $C_2H_2O_4 \cdot 2H_2O$ | 1.2851 | 0.7782 |
| $H_2SO_4$ | $C_4H_6O_6$ | 1.5298 | 0.6537 |
| $H_2SO_4$ | $Cl_2$ | 0.7230 | 1.3831 |
| $H_2SO_4$ | $CO_2$ | 0.4487 | 2.2287 |
| $H_2SO_4$ | $CuSO_4$ | 1.6275 | 0.6144 |
| $H_2SO_4$ | Fe | 0.5203 | 1.9220 |
| $H_2SO_4$ | FeO | 0.7324 | 1.3653 |
| $H_2SO_4$ | $Fe_2O_3$ | 0.5427 | 1.8428 |
| $H_2SO_4$ | FeS | 0.8963 | 1.1155 |
| $H_2SO_4$ | $FeSO_4$ | 1.5487 | 0.6457 |
| $H_2SO_4$ | $FeSO_4 \cdot 7H_2O$ | 2.8345 | 0.3528 |
| $H_2SO_4$ | $Fe_2(SO_4)_3$ | 1.3590 | 0.7358 |
| $H_2SO_4$ | $H_3AsO_4$ | 0.9648 | 1.0365 |
| $H_2SO_4$ | HCl | 0.7436 | 1.3448 |
| $H_2SO_4$ | $H_2C_2O_4$ | 0.9177 | 1.0898 |
| $H_2SO_4$ | $HCO_2H$ | 0.9383 | 1.0658 |
| $H_2SO_4$ | HF | 0.4080 | 2.4510 |
| $H_2SO_4$ | $HNO_2$ | 0.9587 | 1.0431 |
| $H_2SO_4$ | $HNO_3$ | 1.2850 | 0.7782 |
| $H_2SO_4$* | $H_3PO_4$ | 0.9998 | 1.0002 |
| $H_2SO_4$* | $H_2S$ | 0.6950 | 1.4388 |
| $H_2SO_4$* | $H_2SO_3$ | 0.8369 | 1.1949 |

A×A′=B and B×B′=A

* Phenolphthalein.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ | A | B | A′ | B′ |
|---|---|---|---|---|---|---|---|
| $H_2SO_4$ | $H_2SiF_6$ | 0.4904 | 2.0391 | I | KI | 1.3081 | 0.7645 |
| $H_2SO_4$ | $K_2Al_2(SO_4)_4 \cdot 24H_2O$ | 3.2253 | 0.3101 | I | $KIO_3$ | 1.6863 | 0.5930 |
| | | | | I | $NaIO_3$ | 1.55 4 | 0.6413 |
| $H_2SO_4$ | $KHC_4H_4O_6$ | 3.8362 | 0.2607 | I | $Na_2SO_3$ | 0.4967 | 2.0135 |
| $H_2SO_4$ | $KNO_3$ | 2.0617 | 0.4850 | I | Pd | 0.4203 | 2.3790 |
| $H_2SO_4$ | $K_2O$ | 0.9604 | 1.0413 | I | $PdI_2$ | 1.4204 | 0.7040 |
| $H_2SO_4$ | KOH | 1.1442 | 0.8740 | I | Tl | 2.6074 | 0.3835 |
| $H_2SO_4$ | $K_2SiF_6$ | 0.7493 | 1.3345 | | | | |
| $H_2SO_4$ | $K_2SO_4$ | 1.7767 | 0.5628 | In | $In_2O_3$ | 1.2090 | 0.8271 |
| $H_2SO_4$ | MgO | 0.4111 | 2.4325 | In | $In_2S_3$ | 1.4187 | 0.7047 |
| $H_2SO_4$ | $MgSO_4$ | 1.2274 | 0.8147 | | | | |
| $H_2SO_4$ | NaCl | 1.1920 | 0.8389 | Ir | $Ir_2O_3$ | 1.2491 | 0.8006 |
| $H_2SO_4$† | $Na_2CO_3$ | 1.0808 | 0.9252 | | | | |
| $H_2SO_4$ | $Na_2C_2O_4$ | 1.3661 | 0.7320 | K | $K_2O$ | 1.2046 | 0.8302 |
| $H_2SO_4$ | $Na_2Cr_2O_7$ | 2.6711 | 0.3744 | K | $K_2PtCl_6$ | 6.2143 | 0.1609 |
| $H_2SO_4$† | $NaHCO_3$ | 1.7132 | 0.5837 | K | $K_2SO_4$ | 2.2285 | 0.4487 |
| $H_2SO_4$* | $NaH_2PO_4$ | 2.4583 | 0.4068 | $K_2Al_2(SO_4)_3 \cdot 24H_2O$ | Al | 0.0571 | 17.510 |
| $H_2SO_4$† | $Na_2HPO_4$ | 2.8964 | 0.3453 | | $Al_2O_3$ | 0.1077 | 9.2863 |
| $H_2SO_4$ | $NaHSO_3$ | 2.1222 | 0.4712 | ditto | $H_2O$ | 0.4561 | 2.1949 |
| $H_2SO_4$ | $NaNO_3$ | 1.7334 | 0.5769 | ditto | $H_2SO_4$ | 0.3101 | 3.2253 |
| $H_2SO_4$ | $Na_2O$ | 0.6321 | 1.5820 | ditto * | $H_2SO_4$ | 0.4134 | 2.4190 |
| $H_2SO_4$ | NaOH | 0.8158 | 1.2258 | ditto (total) | $H_2SO_4$ (+Al +K) | | |
| $H_2SO_4$ | $Na_3PO_4$ | 3.3448 | 0.2990 | | | | |
| $H_2SO_4$ | $Na_2S$ | 0.7959 | 1.2564 | ditto | S | 0.1352 | 7.3984 |
| $H_2SO_4$ | $Na_2SiF_6$ | 0.9598 | 1.0418 | ditto | K | 0.0824 | 12.1363 |
| $H_2SO_4$ | $Na_2SO_3$ | 2.5706 | 0.3 90 | $K_2Al_2(SO_4)_3$ | $NaHCO_3$ | 0.9756 | 1.0251 |
| $H_2SO_4$ | $Na_2SO_4$ | 1.4404 | 0.6904 | $KBF_4$ | $Na_2B_4O_7 \cdot 10H_2O$ | 0.7570 | 1.3199 |
| $H_2SO_4$ | $NH_3$ | 0.3473 | 2.8792 | | | | |
| $H_2SO_4$ | $NH_4Cl$ | 1.0909 | 0.9167 | KBr | Br | 0.6715 | 1.4892 |
| $H_2SO_4$ | $(NH_4)_2O$ | 0.5310 | 1.8382 | KBr | K | 0.3285 | 3.0440 |
| $H_2SO_4$ | $(NH_4)_2S$ | 0.6948 | 1.4392 | KCl | Ag | 1.4469 | 0.6911 |
| $H_2SO_4$ | $(NH_4)_2SO_4$ | 1.3473 | 0.7422 | KCl | AgCl | 1.9225 | 0.5202 |
| $H_2SO_4$ | $(NH_4)_2S_2O_8$ | 2.3268 | 0.4298 | KCl | Cl | 0.4756 | 2.1027 |
| $H_2SO_4$ | $N_2O_3$ | 0.7750 | 1.2903 | KCl | HCl | 0.4891 | 2.0445 |
| $H_2SO_4$ | $N_2O_4$ | 0.9382 | 1.0659 | KCl | $KHC_4H_4O_6$ | 2.5233 | 0.3963 |
| $H_2SO_4$ | $N_2O_5$ | 1.1013 | 0.9080 | KCl | $K_2PtCl_4$ | 3.2589 | 0.3069 |
| $H_2SO_4$‡ (Y ppt.) | P | 0.0275 | 36.364 | KCl | $K_2SO_4$ | 1.1686 | 0.8557 |
| | | | | KCl | Pt | 2.4935 | 0.4010 |
| $H_2SO_4$ | $P_2O_5$ | 0.7243 | 1.3806 | $KClO_3$ | AgCl | 1.1696 | 0.8550 |
| $H_2SO_4$‡ (Y ppt.) | $P_2O_5$ | 0.0629 | 15.878 | KCN | AgCN | 2.0564 | 0.4863 |
| | | | | KCN | AgCl | 1.1696 | 0.8550 |
| $H_2SO_4$ | S | 0.3267 | 3.0590 | $K_2CO_3$ | $CO_2$ | 0.3184 | 3.1409 |
| $H_2SO_4$† | $SO_2$ | 0.6532 | 1.5309 | $K_2CO_3$ | KOH | 0.8120 | 1.2315 |
| $H_2SO_4$* | $SO_3$ | 1.3064 | 0.7655 | $K_2CO_3$ | $K_2SO_4$ | 1 2610 | 0.7930 |
| $H_2SO_4$ | $SO_3$ | 0.8163 | 1.2250 | $K_2CrO_4$ | $BaCrO_4$ | 1.3046 | 0.7666 |
| $H_2SO_4$ | $S_2O_5Cl_2$ | 0.7309 | 1.3683 | $K_2CrO_4$ | $CrO_3$ | 0.5153 | 1.9411 |
| $H_2SO_4$ | $SO_2HCl$ | 0.7921 | 1.2625 | $K_2Cr_2O_7$ | $BaCrO_4$ | 1.7220 | 0.5807 |
| $H_2SO_4$ | Zn | 0.6665 | 1.5004 | $K_2Cr_2O_7$ | $CrO_3$ | 0.6800 | 1.4706 |
| $H_2SO_4$ | ZnO | 0.8296 | 1.2054 | $K_2Cr_2O_7$ | Fe | 1.1388 | 0.8782 |
| $H_2SO_4$ | $ZnSO_4$ | 1.6459 | 0.6076 | $K_2Cr_2O_7$ | $K_2O$ | 0.3200 | 3.1252 |
| | | | | KHCO | $CO_2$ | 0.4395 | 2.2752 |
| I | AgI | 1.8500 | 0.5405 | $KHSO_4$ | $BaSO_4$ | 1.7141 | 0.5834 |
| I | Cl | 0.2794 | 3.5792 | KI | I | 0.7645 | 3.0440 |

A×A′=B and B×B′=A.

* Phenolphthalein. † Methyl Orange.

‡ Titration of yellow precipitate, ammonium phosphomolybdate.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ | A | B | A′ | B′ |
|---|---|---|---|---|---|---|---|
| KI | K | 0.2355 | 4.2460 | La | $La_2O_3$ | 1.1727 | 0.8528 |
| $KMnO_4$ | $Mn_3O_4$ | 0.4826 | 2.0721 | | | | |
| $KNO_3$ | $H_2SO_4$ | 0.4850 | 2.0617 | Li | LiCl | 6.1096 | 0.1637 |
| $KNO_3$ | $K_2PtCl_6$ | 2.4041 | 0.4159 | Li | $Li_2CO_3$ | 5.3227 | 0.1879 |
| $KNO_3$ | $NaNO_3$ | 0.8408 | 1.1894 | Li | $Li_2O$ | 2.1539 | 0.4643 |
| $KNO_3$ | NO | 0.2968 | 3.6898 | Li | $Li_2PO_4$ | 5.5629 | 0.1798 |
| $KNO_3$ | $N_2O_5$ | 0.5342 | 1.8721 | LiCl | $Li_2SO_4$ | 7.1296 | 0.1262 |
| KOH | $H_2SO_4$ | 0.8741 | 1.1440 | LiCl | $Li_2O$ | 0.3523 | 2.8381 |
| KOH | $K_2CO_3$ | 1.2315 | 0.8120 | $Li_2O$ | $Li_2CO_3$ | 2.4630 | 0.4044 |
| KOH | $K_2O$ | 0.8394 | 1.1913 | $Li_2O$ | $Li_2SO_4$ | 3.6799 | 0.2718 |
| $K_2O$ | Cl | 0.7529 | 1.3282 | $Li_2O$ | $Li_3PO_4$ | 2.5842 | 0.3870 |
| $K_2O$ | $CO_2$ | 0.4671 | 2.1409 | $Li_3PO_4$ | $Li_2CO_3$ | 0.9569 | 1.0451 |
| $K_2O$ | HCl | 0.7743 | 1.2915 | $Li_3PO_4$ | $LiHCO_3$ | 1.7601 | 0.5682 |
| $K_2O$ | $H_2SO_4$ | 1.0413 | 0.9604 | $Li_3PO_4$ | $Li_2SO_4$ | 1.4240 | 0.7023 |
| $K_2O$ | K | 2.8302 | 1.2046 | $Li_2SO_4$ | Li | 0.1262 | 7.9216 |
| $K_2O$ | KBr | 2.5270 | 0.3957 | $Li_2SO_4$ | LiCl | 0.7712 | 1.2966 |
| $K_2O$ | KCl | 1.5830 | 0.6317 | $Li_2SO_4$ | $SO_3$ | 0.7282 | 1.3732 |
| $K_2O$ | $KHCO_3$ | 1.0627 | 0.9410 | | | | |
| $K_2O$ | $K_2CO_3$ | 1.4671 | 0.6816 | Mg | Cl | 2.9162 | 0.3429 |
| $K_2O$ | $KHC_4H_4O_6$ | 3.9936 | 0.2504 | Mg | MgO | 1.6579 | 0.6032 |
| $K_2O$ | $K_2Cr_2O_7$ | 3.1252 | 0.3200 | Mg | $Mg_2P_2O_7$ | 4.5789 | 0.2184 |
| $K_2O$ | KI | 3.5248 | 0.2837 | Mg | $MgSO_4$ | 4.9450 | 0.2020 |
| $K_2O$ | KOH | 1.1913 | 0.8394 | $MgCl_2$ | Cl | 0.7447 | 1.3429 |
| $K_2O$ | $KNO_3$ | 2.1466 | 0.4658 | $MgCl_2 \cdot 6H_2O$ | Cl | 0.3488 | 2.8672 |
| $K_2O$ | $K_2PtCl_6$ | 5.1609 | 0.1938 | $MgCO_3$ | $CO_2$ | 0.5218 | 1.9164 |
| $K_2O$ | $K_2SO_4$ | 1.8500 | 0.5406 | $Mg(HCO_3)_2$ | $CO_2$ | 0.6013 | 1.6629 |
| $K_2O$ | $SO_3$ | 0.8500 | 1.1765 | MgO | $BaSO_4$ | 5.7897 | 0.1727 |
| $K_2PtCl_6$ | K | 0.1609 | 6.2143 | MgO | Cl | 1.7590 | 0.5685 |
| $K_2PtCl_6$ | KCl | 0.3068 | 3.2589 | MgO | $CO_2$ | 1.0913 | 0.9164 |
| $K_2PtCl_6$ | $K_2CO_3$ | 0.2844 | 3.5162 | MgO | $H_2SO_4$ | 2.4325 | 0.4111 |
| $K_2PtCl_6$ | $KNO_3$ | 0.4159 | 2.4041 | MgO | $MgCl_2$ | 2.3621 | 0.4234 |
| $K_2PtCl_6$ | $K_2O$ | 0.1938 | 5.1609 | MgO | $MgCO_3$ | 2.0913 | 0.4782 |
| $K_2PtCl_6$ | $K_2SO_4$ | 0.3585 | 2.7897 | MgO | $Mg(HCO_3)_2$ | 3.6294 | 0.2755 |
| $K_2PtCl_6$ | $K_2Al_2(SO_4)_4 \cdot 24H_2O$ | 1.9530 | 0.5120 | MgO | $Mg_2P_2O_7$ | 2.7619 | 0.3621 |
| $K_2PtCl_6$ | $K_2Cr_2(SO_4)_4 \cdot 24H_2O$ | 2.0559 | 0.4964 | MgO | $MgSO_4$ | 2.9859 | 0.3349 |
| | | | | MgO | $Na_2SO_4$ | 3.5236 | 0.2838 |
| $K_2PtCl_6$ | Pt | 0.4013 | 2.4921 | MgO | S | 0.7954 | 1.2572 |
| $K_2PtCl_6$ | $PtCl_4$ | 0 6931 | 1.4427 | MgO | $SO_3$ | 1.9859 | 0.5036 |
| $K_2PtCl_6$ | $PtCl_4 \cdot 5H_2O$ | 0.8785 | 1.1383 | $Mg_2P_2O_7$ | $Ca_3(PO_4)_2$ | 1.3932 | 0.7178 |
| $K_2SiF_6$ | F | 0.5170 | 1.9342 | $Mg_2P_2O_7$ | $H_3PO_4$ | 0.8806 | 1.1356 |
| $K_2SiF_6$ | HF | 0.5444 | 1.8368 | $Mg_2P_2O_7$ | Mg | 0.2184 | 4.5789 |
| $K_2SiF_6$ | $H_2SiF_6$ | 0.6545 | 1.5276 | $Mg_2P_2O_7$ | $Mg(CH_3CO_2)$ | 1.2784 | 0.7822 |
| $K_2SiF_6$ | $H_2SO_4$ | 1.3345 | 0.7493 | $Mg_2P_2O_7$ | $MgCl_2$ | 0.8552 | 1.1692 |
| $K_2SiF_6$ | KF | 0.5270 | 1.8976 | $Mg_2P_2O_7$ | $MgCl_2 \cdot 6H_2O$ | 1.8260 | 0.5477 |
| $K_2SiF_6$ | $SiF_4$ | 0.4730 | 2.1141 | $Mg_2P_2O_7$ | $MgCO_3$ | 0.7575 | 1.3203 |
| $K_2SiF_6$ | $SiO_2$ | 0.2735 | 3.6567 | $Mg_2P_2O_7$ | $Mg(HCO_3)_2$ | 1.3141 | 0.7610 |
| $K_2SiO_3$ | $SiO_2$ | 0.3903 | 2.5622 | $Mg_2P_2O_7$ | MgO | 0.3621 | 2.7619 |
| $K_2SO_4$ | $H_2SO_4$ | 0.5628 | 1.7767 | $Mg_2P_2O_7$ | $MgSO_4$ | 1.0811 | 0.9250 |
| $K_2SO_4$ | K | 0.4487 | 2.2285 | $Mg_2P_2O_7$ | $MgSO_4 \cdot 7H_2O$ | 2.2143 | 0.4516 |
| $K_2SO_4$ | KCl | 0.8557 | 1.1686 | $Mg_2P_2O_7$ | $Na_3PO_4$ | 1.4731 | 0.6789 |
| $K_2SO_4$ | $K_2CO_3$ | 0.7930 | 1.2610 | $Mg_2P_2O_7$ | $Na_2HPO_4$ | 1.2755 | 0.7840 |
| $K_2SO_4$ | $K_2O$ | 0.5405 | 1.8500 | $Mg_2P_2O_7$ | $Na_2SO_4$ | 1.2758 | 0.7838 |
| $K_2SO_4$ | $K_2PtCl_6$ | 2.7897 | 0.3585 | $Mg_2P_2O_7$ | $(NH_4)_2FO_4$ | 1.0336 | 0.9675 |
| $K_2SO_4$ | $SO_3$ | 0.4595 | 2.1765 | $Mg_2P_2O_7$ | $(NH_4)_2HPO_4$ | 1.1865 | 0.8428 |
| | | | | $Mg_2P_2O_7$ | P | 0.2787 | 3.5877 |

$A \times A' = B$ and $B \times B' = A$.

## TABLES AND USEFUL DATA

VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ | A | B | A′ | B′ |
|---|---|---|---|---|---|---|---|
| $Mg_2P_2O_7$ | $P_2O_5$ | 0.6379 | 1.5676 | Na | NaI | 6.5183 | 0.1534 |
| $MgSO_4$ | $BaSO_4$ | 1.9389 | 0.5158 | Na | $Na_2O$ | 1.3478 | 0.7419 |
| $MgSO_4$ | $H_2SO_4$ | 0.8147 | 1.2274 | Na | NaOH | 1.7391 | 0.5750 |
| $MgSO_4$ | $SO_3$ | 0.6651 | 1.5036 | Na | $Na_2SO_3$ | 2.6754 | 0.3738 |
| $MgSO_4 \cdot 7H_2O$ | $SO_3$ | 0.3248 | 3.0786 | Na | $Na_2SO_4$ | 3.0885 | 0.3238 |
| $MgSO_4 \cdot 7H_2O$ | $BaSO_4$ | 0.9469 | 1.056 | $Na_2Al_2O_4$ | $Al_2O_3$ | 0.6224 | 1.6067 |
| | | | | $Na_2Al_2(SO_4)_4$ | | | |
| Mn | $MnCO_3$ | 2.0923 | 0.4779 | $\cdot 24H_2O$ | S | 0.1399 | 7.1474 |
| Mn | MnO | 1.2913 | 0.7744 | $Na_2B_4O_7$ | $B_2O_3$ | 0.6931 | 1.4429 |
| Mn | $Mn_2O_3$ | 1.4369 | 0.6959 | $Na_2B_4O_7$ | $H_3BO_3$ | 1.2282 | 0.8142 |
| Mn | $Mn_3O_4$ | 1.3884 | 0.7203 | $Na_2B_4O_7$ | | | |
| Mn | $Mn_2P_2O_7$ | 2.5846 | 0.3869 | $\cdot 10H_2O$ | $B_2O_3$ | 0.1832 | 5.4594 |
| Mn | MnS | 1.5838 | 0.6314 | ditto | $H_3BO_3$ | 0.6492 | 1.5404 |
| $MnCO_3$ | $CO_2$ | 0.3828 | 2.6121 | ditto | KBF | 1.3199 | 0.7577 |
| $Mn(HCO_3)_2$ | $CO_2$ | 0.4973 | 2.0108 | NaBr | Ag | 1.0458 | 0.9562 |
| MnO | $MnCO_3$ | 1.6203 | 0.6172 | NaBr | AgBr | 1.8247 | 0.5480 |
| MnO | $Mn_2O_3$ | 1.1128 | 0.8987 | NaBr | Br | 0.7765 | 1.2878 |
| MnO | MnS | 1.2266 | 0.8153 | NaCl | A Cl | 2.4519 | 0.4078 |
| MnO | $SO_3$ | 1.1289 | 0.8859 | NaCl | $AgNO_3$ | 2.9061 | 0.3441 |
| $Mn_2O_3$ | $KMnO_4$ | 2.0721 | 0.4826 | NaCl | CaO | .4786 | 2.0852 |
| $Mn_2O_3$ | $Mn_3O_4$ | 0.9662 | 1.0349 | NaCl | Cl | 0.6066 | 1.6486 |
| $Mn_2O_3$ | $MnSO_4$ | 2.0398 | 0.4902 | NaCl | HCl | 0.6239 | 1.6030 |
| $Mn_2O_3$ | S | 0.2032 | 4.9224 | NaCl | $H_2SO_4$ | 0.8389 | 1.1920 |
| $Mn_3O_4$ | $K_2MnO_4$ | 2.5848 | 0.3869 | NaCl | $Na_2CO_3$ | 0.9066 | 1.1030 |
| $MnSO_4$ | $BaSO_4$ | 1.5458 | 0.6469 | NaCl | $NaHCO_3$ | 1.4370 | 0.6959 |
| $MnSO_4$ | $SO_3$ | 0.5303 | 1.8858 | NaCl | $Na_2HPO_4$ | 1.2149 | 0.8231 |
| | | | | NaCl | $NaHSO_3$ | 1.7803 | 0.5617 |
| Mo | $MoO_3$ | 1.5000 | 0.6657 | NaCl | $Na_2O$ | 0.5303 | 1.8858 |
| Mo | $MoS_2$ | 2.0022 | 0.4995 | NaCl | $Na_2SO_4$ | 1.2151 | 0.8230 |
| Mo | $PbMoO_4$ | 3.8239 | 0.2615 | NaCl | $ZnCl_2$ | 1.1656 | 0.8579 |
| $MoO_3$ | $MoS_2$ | 1.3348 | 0.7492 | $NaClO_3$ | Cl | 0.3331 | 3.0023 |
| $MoO_3$ | $(NH_4)_2MoO_4$ | 1.3617 | 0.7344 | $NaClO_4$ | Cl | 0.2896 | 3.4535 |
| $MoO_3$ | $(NH_4)_3PO_4$ | | | $Na_2CO_3$ | $BaSO_4$ | 2.2022 | 0.4541 |
| | $(MoO_3)_{12}$ | 1.0863 | 0.9205 | $Na_2CO_3$ | $CaCO_3$ | 0.9441 | 1.0593 |
| $MoO_3$ | $PbMoO_4$ | 2.5494 | 0.3923 | $Na_2CO_3$ | CaO | 0.5290 | 1.8905 |
| $MoO_4 \cdot (NH_4)_2$ | $PbMoO_4$ | 1.8722 | 0.5342 | $Na_2CO_3$ | $CH_3CO_2H$ | 1.1327 | 0.8828 |
| | | | | $Na_2CO_3$ | $CO_2$ | 0.4151 | 2.4091 |
| N | $HNO_3$ | 4.4981 | 0.2223 | $Na_2CO_3$ | HCl | 0.6881 | 1.4533 |
| N | $NO_2$ | 3.2841 | 0.3045 | $Na_2CO_3$ | $H_2SO_4$ | 0.9253 | 1.0807 |
| N | $N_2O_3$ | 2.7131 | 0.3686 | $Na_2CO_3$ | Na | 0.4340 | 2.3044 |
| N | $N_2O_4$ | 3.2841 | 0.3045 | $Na_2CO_3$ | NaCl | 1.1030 | 0.9066 |
| N | $N_2O_5$ | 3.8551 | 0.2594 | $Na_2CO_3$ | $NaHCO_3$ | 0.7925 | 1.2618 |
| N | $NaNO_3$ | 6.0678 | 0.1648 | $Na_2CO_3$ | $NaHSO_3$ | 1.9637 | 0.5092 |
| N | $NH_3$ | 1.2155 | 0.8227 | $Na_2CO_3$ | NaOH | 0.7549 | 1.3247 |
| N | Pt | 6.9665 | 0.1435 | $Na_2CO_3$ | $Na_2O$ | 0.5849 | 1.7097 |
| N | $SO_3$ | 2.8576 | 0.3499 | $Na_2C_2O_4$ | $H_2SO_4$ | 0.7320 | 1.3661 |
| | | | | $Na_2CrO_4$ | $PbCrO_4$ | 1.9944 | 0.5014 |
| Na | Br | 3.4748 | 0.2878 | $Na_2Cr_2O_7$ | Fe | 1.2788 | 0.7820 |
| Na | Cl | 1.5417 | 0.6486 | $Na_2Cr_2O_7$ | $H_2SO_4$ | 0.3744 | 2.6711 |
| Na | I | 5.5182 | 0.1812 | $Na_2Cr_2O_7$ | $Na_2CrO_4$ | 1.2367 | 0.8086 |
| Na | NaBr | 4.4747 | 0.2235 | NaF | $CaF_2$ | 0.9294 | 1.0760 |
| Na | NaCl | 2.5417 | 0.3934 | $Na_2HAsO_3$ | $Mg_2As_2O_7$ | 0.9135 | 1.0947 |
| Na | $Na_2CO_3$ | 2.3044 | 0.4340 | $Na_2HAsO_4$ | As | 0.4031 | 2.4809 |
| Na | NaF | 1.8261 | 0.5476 | $Na_2HAsO_4$ | $As_2O_5$ | 0.6182 | 1.6177 |
| Na | $NaHCO_3$ | 3.6525 | 0.2740 | $Na_2HAsO_4$ | $Mg_2As_2O_7$ | 0.8349 | 1.1978 |

$A \times A' = B$ and $B \times B' = A$.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ | A | B | A′ | B′ |
|---|---|---|---|---|---|---|---|
| $Na_2HAsO_4$ | $As_2O_5$ | 0.7011 | 1.4264 | $NaNO_3$ | $NH_3$ | 0.2004 | 4.9906 |
| $NaHCO_3$ | $Al_2(SO_4)_3$ | 0.6793 | 1.4721 | $NaNO_3$ | NO | 0.3530 | 2.8327 |
| $NaHCO_3$* | $Ca(H_2PO_4)_2$ | 1.3938 | 0.7175 | $NaNO_3$ | $N_2O_5$ | 0.6353 | 1.5740 |
| $NaHCO_3$* | $CaH_2P_2O_7$ | 1.2866 | 0.7773 | NaOH | $H_2SO_4$ | 1.2258 | 0.8158 |
| $NaHCO_3$ | $C_4H_6O_6$ | 0.8931 | 1.1197 | NaOH | $Na_2O$ | 0.7748 | 1.2906 |
| $NaHCO_3$ | $CO_2$ | 0.5238 | 1.9039 | NaOH | $Na_2SiF_6$ | 0.8499 | 1.1766 |
| $NaHCO_3$ | $H_2SO_4$ | 0.5838 | 1.7129 | NaOH | $(NH_4)_3PO_4$ $\cdot(MoO_3)_{12}$ | 2.0400 | 0.4902 |
| $NaHCO_3$ | $K_2Al_2(SO_4)_4$ | 1.0251 | 0.9756 | | | | |
| $NaHCO_3$ | $KHC_4H_4O_6$ | 2.2395 | 0.4465 | $Na_2O$ | $BaSO_4$ | 3.7651 | 0.2656 |
| $NaHCO_3$ | $KMnO_4$ | 0.4717 | 2.1260 | $Na_2O$ | $CH_3CO_2H$ | 1.9365 | 0.5164 |
| $NaHCO_3$ | Na | 0.2740 | 3.6525 | $Na_2O$ | $CH_3CO_2Na$ | 2.6459 | 0.3779 |
| $NaHCO_3$ | $Na_2CO_3$ | 1.2618 | 0.7925 | $Na_2O$ | $H_2SO_4$ | 1.582 | 0.6321 |
| $NaHCO_3$* | $NaH_2PO_4$ | 1.4291 | 0.6997 | $Na_2O$ | Na | 0.7419 | 1.3478 |
| $NaHCO_3$* | $Na_2H_2P_2O_4$ | 1.3219 | 0.7565 | $Na_2O$ | NaCl | 1.8858 | 0.5303 |
| $NaHCO_3$ | $Na_2O$ | 0.3690 | 2.7099 | $Na_2O$ | $Na_2CO_3$ | 1.7097 | 0.5849 |
| $NaH_2PO_4$* | $H_2SO_4$ | 0.4068 | 2.4583 | $Na_2O$ | NaF | 1.3548 | 0.7381 |
| $NaH_2PO_4$* | $NaHCO_3$ | 0.6997 | 1.4291 | $Na_2O$ | $NaHCO_3$ | 2.7099 | 0.3690 |
| $NaH_2PO_4$* | $NaH_2PO_4$ $\cdot 4H_2O$ | 1.6003 | 0.6249 | $Na_2O$ | $Na_2HPO_4$ | 2.2911 | 0.4365 |
| | | | | $Na_2O$ | $NaH_2PO_4$ | 3.8728 | 0.2582 |
| $NaH_2PO_4$* | $Na_2O$ | 0.2582 | 3.8728 | $Na_2O$ | $Na_2H_2P_2O_7$ | 3.5822 | 0.2792 |
| $NaH_2PO_4$* | P | 0.2585 | 3.8678 | $Na_2O$ | $NaHSO_3$ | 3.3574 | 0.2979 |
| $NaH_2PO_4$* | $P_2O_5$ | 0.5917 | 1.6900 | $Na_2O$ | $NaNO_3$ | 2.7423 | 0.3647 |
| $Na_2HPO_4$† | $H_2SO_4$ | 0.3453 | 2.8964 | $Na_2O$ | NaOH | 1.2906 | 0.7748 |
| $Na_2HPO_4$ | $Na_2HPO_4$ $\cdot 12H_2O$ | 2.5220 | 0.3965 | $Na_2O$ | $Na_3PO_4$ | 1.7639 | 0.5669 |
| | | | | $Na_2O$ | $Na_2S$ | 1.2592 | 0.7942 |
| $Na_2HPO_4$ | $Na_2O$ | 0.4365 | 2.2911 | $Na_2O$ | $Na_2SO_3$ | 2.0334 | 0.4918 |
| $Na_2HPO_4$ | $P_2O_5$ | 0.5001 | 1.9995 | $Na_2O$ | $Na_2SO_4$ | 2.2915 | 0.4364 |
| $Na_2H_2P_2O_7$ | $NaHCO_3$ | 0.7565 | 1.3219 | $Na_2O$* | $P_2O_5$ | 1.1458 | 0.8727 |
| $Na_2H_2P_2O_7$ | $Na_2O$ | 0.2792 | 3.5822 | $Na_2O$ | $SO_3$ | 1.2915 | 0.7743 |
| $Na_2H_2P_2O_7$ | $P_2O_5$ | 0.6397 | 1.5632 | $Na_2S$ | $BaSO_4$ | 2.9904 | 0.3344 |
| $Na(NH_4)$ $HPO_4 \cdot 4H_2O$ | $P_2O_5$ | 0.3395 | 2.9452 | $Na_2S$ | $H_2S$ | 0.4237 | 2.3602 |
| | | | | $Na_2S$ | $H_2SO_4$ | 1.2564 | 0.7959 |
| $Na_3PO_4$ | $H_2SO_4$ | 0.2990 | 3.3448 | $Na_2S$ | $Na_2O$ | 0.7942 | 1.2592 |
| $Na_3PO_4$ | $Mg_2P_2O_7$ | 0.6789 | 1.4731 | $Na_2S$ | S | 0.4108 | 2.4343 |
| $Na_3PO_4$ | $Na_2O$ | 0.5669 | 1.7639 | $Na_2SO_3$ | $BaSO_4$ | 1.8515 | 0.5401 |
| $Na_3PO_4$ | $Na_2SO_4$ | 1.2991 | 0.7698 | $Na_2SO_3$ | $H_2SO_4$ | 0.3890 | 2.5706 |
| $Na_3PO_4$ | $Na_3PO_4$ $\cdot 12H_2O$ | 2.3179 | 0.4314 | $Na_2SO_3$ | I | 2.0135 | 0.4966 |
| | | | | $Na_2SO_3$ | $Na_2O$ | 0.4918 | 2.0334 |
| $Na_3PO_4$ | $P_2O_5$ | 0.4331 | 2.3091 | $Na_2SO_3$ | $SO_2$ | 0.5082 | 1.9677 |
| $NaHSO_3$ | $BaSO_4$ | 2.2432 | 0.4485 | $Na_2SO_4 \cdot 7H_2O$ | $SO_2$ | 0.2541 | 3.9360 |
| $NaHSO_3$ | $H_2SO_4$ | 0.4712 | 2.1222 | $Na_2S_2O_3$ | $BaSO_4$ | 2.9524 | 0.3387 |
| $NaHSO_3$ | NaCl | 0.5617 | 1.7803 | $Na_2S_2O_3$ | $Na_2S_2O_3$ $\cdot 5H_2O$ | 1.5696 | 0.6371 |
| $NaHSO_3$ | $Na_2O$ | 0.2979 | 3.3574 | | | | |
| $NaHSO_3$ | $Na_2S_2O_5$ | 0.9134 | 1.0948 | $Na_2SO_4$ | $BaSO_4$ | 1.6431 | 0.6086 |
| $NaHSO_3$ | $SO_2$ | 6.6156 | 1.6244 | $Na_2SO_4$ | CaO | 0.3947 | 2.5338 |
| NaI | Na | 0.1534 | 6.5183 | $Na_2SO_4$ | $CH_3CO_2Na$ | 1.1547 | 0.8660 |
| NaI | $Na_2O$ | 0.2068 | 4.8350 | $Na_2SO_4$ | $H_2SO_4$ | 0.6904 | 1.4484 |
| $NaIO_3$ | I | 0.6413 | 1.5594 | $Na_2SO_4$ | MgO | 0.2838 | 3.5236 |
| $NaNO_3$ | $HNO_3$ | 0.7413 | 1.3490 | $Na_2SO_4$ | $Mg_2P_2O_7$ | 0.7838 | 1.2758 |
| $NaNO_3$ | $H_2SO_4$ | 0.5769 | 1.7334 | $Na_2SO_4$ | Na | 0.3238 | 3.0835 |
| $NaNO_3$ | $KNO_3$ | 1.1894 | 0.8408 | $Na_2SO_4$ | NaCl | 0.8230 | 1.2151 |
| $NaNO_3$ | $NaNO_2$ | 0.8117 | 1.2319 | $Na_2SO_4$ | $Na_2CO_3$ | 0.7461 | 1.3403 |
| $NaNO_3$ | $Na_2O$ | 0.3647 | 2.7423 | $Na_2SO_4$ | NaF | 0.5913 | 1.6905 |

$A \times A' = B$ and $B \times B' = A$.

* Phenolphthalein. † Methyl Orange.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ |
|---|---|---|---|
| $Na_2SO_4$ | $NaHSO_3$ | 1.4652 | 0.6825 |
| $Na_2SO_4$ | $Na_2O$ | 0.4364 | 2.2915 |
| $Na_2SO_4$ | $Na_2S$ | 0.5495 | 1.8198 |
| $Na_2SO_4$ | $Na_2S_2O_3$ | 0.8874 | 1.1269 |
| $Na_2SO_4$ | $Na_2SO_4 \cdot 10H_2O$ | 2.2681 | 0.4409 |
| $Na_2SO_4$ | $SO_3$ | 0.5636 | 1.7743 |
| Nd | $Nd_2O_3$ | 1.1674 | 0.8566 |
| $NH_3$ | $HNO_3$ | 3.6995 | 0.2704 |
| $NH_3$ | $H_2SO_4$ | 2.8792 | 0.3473 |
| $NH_3$ | N | 0.8227 | 1.2155 |
| $NH_3$ | $NaNO_2$ | 4.0513 | 0.2468 |
| $NH_3$ | $NaNO_3$ | 4.9906 | 0.2005 |
| $NH_3$ | $NH_4Cl$ | 3.1409 | 0.3184 |
| $NH_3$ | $(NH_4)_2HPO_4$ | 3.8785 | 0.2578 |
| $NH_3$ | $(NH_4)H_2PO_4$ | 6.7570 | 0.1480 |
| $NH_3$ | $NH_4OH$ | 2.0577 | 0.4860 |
| $NH_3$ | $(NH_4)_2PtCl_6$ | 13.032 | 0.0764 |
| $NH_3$ | $(NH_4)_2SO_4$ | 3.8790 | 0.2578 |
| $NH_3$ | $N_2O_5$ | 3.1714 | 0.3153 |
| $(NH_4)_2Al_2(SO_4)_4 \cdot 24H_2O$ | $Al_2O_3$ | 0.1127 | 8.8742 |
| ditto | S | 0.1414 | 7.0696 |
| $NH_4Cl$ | AgCl | 2.6793 | 0.3732 |
| $NH_4Cl$ | Cl | 0.6628 | 1.5088 |
| $NH_4Cl$ | HCl | 0.6817 | 1.4669 |
| $NH_4Cl$ | $H_2SO_4$ | 0.9167 | 1.0909 |
| $(NH_4)H_2PO_4$ | $Mg_2P_2O_7$ | 0.9675 | 1.0336 |
| $(NH_4)H_2PO_4$ | $NH_3$ | 0.1480 | 6.7570 |
| $(NH_4)_2HPO_4$ | $Mg_2P_2O_7$ | 0.8428 | 1.1865 |
| $(NH_4)_2HPO_4$ | $NH_3$ | 0.2578 | 3.8785 |
| $(NH_4)_2O$ | $H_2SO_4$ | 1.8832 | 0.5310 |
| $(NH_4)_3PO_4 \cdot (MoO_3)_{12}$ | P | 0.0165 | 60.475 |
| ditto | $P_2O_5$ | 0.0378 | 26.424 |
| $(NH_4)_2PtCl_6$ | $HNO_3$ | 0.2840 | 3.5215 |
| $(NH_4)_2PtCl_6$ | Pt | 0.4393 | 2.2761 |
| $(NH_4)_2PtCl_6$ | $PtCl_4$ | 0.7589 | 1.3177 |
| $(NH_4)_2S$ | $H_2SO_4$ | 1.4392 | 0.6948 |
| $(NH_4)_2SO_4$ | $BaSO_4$ | 1.7665 | 0.5661 |
| $(NH_4)_2SO_4$ | $H_2SO_4$ | 0.7422 | 1.3473 |
| $(NH_4)_2SO_4$ | N | 0.2120 | 4.7162 |
| $(NH_4)_2SO_4$ | $NH_3$ | 0.2578 | 3.8790 |
| $(NH_4)_2SO_4$ | $N_2O_5$ | 0.8174 | 1.2234 |
| $(NH_4)_2S_2O_8$ | $H_2SO_4$ | 0.4298 | 2.3268 |
| Ni | $NiC_4H_8N_4O_4$ | 4.9221 | 0.2032 |
| Ni | $Ni(NO_3)_2 \cdot 6H_2O$ | 4.9556 | 0.2018 |
| Ni | NiO | 1.2727 | 0.7858 |
| Ni | $NiSO_4$ | 2.6371 | 0.3792 |
| Ni | $NiSO_4 \cdot 7H_2O$ | 4.7863 | 0.2089 |
| NO | $HNO_2$ | 1.5667 | 0.6382 |
| NO | $HNO_3$ | 2.0999 | 0.4762 |
| NO | $KNO_3$ | 3.3689 | 0.2968 |
| NO | $NaNO_3$ | 2.8327 | 0.3530 |

1cc NO = 0.0021 g. $HNO_2$, or 0.0028143 g. $HNO_3$, or 0.00415 g. $KNO_3$, or 0.003796 g. $NaNO_3$, or 0.00134 g. NO, or 0.001696 g. $N_2O_3$, or 0.0020545 g. $N_2O_4$.

| A | B | A′ | B′ |
|---|---|---|---|
| $N_2O_3$ | $AgNO_3$ | 4.0487 | 0.2470 |
| $N_2O_3$ | HCl | 0.9594 | 1.0423 |
| $N_2O_3$ | $HNO_3$ | 1.6579 | 0.6032 |
| $N_2O_3$* | $H_2SO_3$ | 1.0798 | 0.9261 |
| $N_2O_3$ | $H_2SO_4$ | 1.2903 | 0.7750 |
| $N_2O_3$ | N | 0.3686 | 2.7131 |
| $N_2O_3$ | $NaNO_2$ | 2.0787 | 0.4810 |
| $N_2O_3$ | NO | 0.7895 | 1.2665 |
| $N_2O_3$ | $N_2O_4$ | 1.2104 | 0.8262 |
| $N_2O_4$ | HCl | 0.7928 | 1.2617 |
| $N_2O_4$ | $HNO_3$ | 1.3697 | 0.7301 |
| $N_2O_4$* | $H_2SO_3$ | 0.9820 | 1.1210 |
| $N_2O_4$ | $H_2SO_4$ | 1.0659 | 0.9382 |
| $N_2O_4$ | N | 0.3045 | 3.2841 |
| $N_2O_4$ | NO | 0.6523 | 1.5332 |
| $N_2O_5$ | HCl | 0.6752 | 1.4810 |
| $N_2O_5$ | $HNO_3$ | 1.1668 | 0.8571 |
| $N_2O_5$* | $H_2SO_3$ | 0.7599 | 1.3159 |
| $N_2O_5$ | $H_2SO_4$ | 0.9080 | 1.1013 |
| $N_2O_5$ | $KNO_3$ | 1.8721 | 0.5342 |
| $N_2O_5$ | $NaNO_3$ | 1.5740 | 0.6353 |
| $N_2O_5$ | $NH_3$ | 0.3153 | 3.1714 |
| $N_2O_5$ | NO | 0.5556 | 1.7997 |
| Os | $OsO_4$ | 1.3353 | 0.7489 |
| P | $H_3PO_4$ | 3.1593 | 0.3165 |
| P | $Mg_2P_2O_7$ | 3.5877 | 0.2787 |
| P | $NaH_2PO_4$ | 3.8678 | 0.2585 |
| P | $(NH_4)_3PO_4 \cdot (MoO_3)_{12}$ | 60.476 | 0.0165 |
| P | $P_2O_5$ | 2.2887 | 0.4369 |
| $P_2O_5$ | $AlPO_4$ | 1.7197 | 0.5815 |
| $P_2O_5$ | $Al_2P_2O_8$ | 1.7193 | 0.5816 |
| $P_2O_5$ | $CaHPO_4$ | 1.9161 | 0.5219 |
| $P_2O_5$ | $Ca(H_2PO_4)_2$ | 1.6483 | 0.6067 |
| $P_2O_5$ | $CaH_2P_2O_7$ | 1.5214 | 0.6573 |
| $P_2O_5$ | $Ca_3P_2O_8$ | 2.1839 | 0.4579 |
| $P_2O_5$ | $FePO_4$ | 2.1239 | 0.4708 |
| $P_2O_5$ | $H_3PO_4$ | 1.3804 | 0.7244 |
| $P_2O_5$ | $H_2SO_4$ | 1.3806 | 0.7243 |

A × A′ = B and B × B′ = A.

* Phenolphthalein.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ |
|---|---|---|---|
| $P_2O_5$ | $Mg_2P_2O_7$ | 1.5676 | 0.6379 |
| $P_2O_5$ | $Na_2HPO_4$ | 1.9995 | 0.5001 |
| $P_2O_5$ | $NaH_2PO_4$ | 1.6900 | 0.5917 |
| $P_2O_5$ | $Na_2H_2P_2O_7$ | 1.5632 | 0.6397 |
| $P_2O_5$ | $Na(NH_4)HPO_4 \cdot 4H_2O$ | 2.9452 | 0.3395 |
| $P_2O_5$* | $Na_2O$ | 0.8727 | 1.1458 |
| $P_2O_5$ | $Na_3PO_4$ | 2.3091 | 0.4331 |
| $P_2O_5$ | $(NH_4)_3PO_4(MoO_3)_{12}$ | 26.424 | 0.0378 |
| Pb | $CH_3CO_2H$ | 0.5797 | 1.7249 |
| Pb | $Pb(C_2H_3O_2)_2$ | 1.5700 | 0.6369 |
| Pb | $PbCl_2$ | 1.3424 | 0.7449 |
| Pb | $PbCO_3$ | 1.2897 | 0.7754 |
| Pb | $(PbCO_3)_2Pb(OH)_2$ | 1.2479 | 0.8014 |
| Pb | $PbCrO_4$ | 1.5601 | 0.6410 |
| Pb | PbO | 1.0773 | 0.9283 |
| Pb | $PbO_2$ | 1.1545 | 0.8662 |
| Pb | $Pb(OH)_2$ | 1.1643 | 0.8589 |
| Pb | PbS | 1.1549 | 0.8659 |
| Pb | $PbSO_4$ | 1.4639 | 0.6831 |
| Pb | S | 0.1548 | 6.4599 |
| $PbCl_2$ | $Cl_2$ | 0.2551 | 3.9202 |
| $PbCO_3$ | $CO_2$ | 0.1547 | 6.0705 |
| $PbCrO_4$ | Cr | 0.1612 | 6.2034 |
| $PbCrO_4$ | $Cr_2O_3$ | 0.2352 | 4.2531 |
| $PbCrO_4$ | $Na_2CrO_4$ | 0.5014 | 1.9944 |
| $PbCrO_4$ | Pb | 0.6410 | 1.5600 |
| $PbCrO_4$ | $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ | 1.1733 | 0.8523 |
| $PbCrO_4$ | $(PbCO_3)_2Pb(OH)_2$ | 0.7996 | 1.2505 |
| $PbCrO_4$ | PbO | 0.6905 | 1.4482 |
| $PbCrO_4$ | $Pb_3O_4$ | 0.7070 | 1.4142 |
| $PbCrO_4$ | $PbSO_4$ | 0.9383 | 1.0657 |
| $PbMoO_4$ | Pb | 0.5642 | 1.7722 |
| $PbMoO_4$ | Mo | 0.2615 | 3.8241 |
| $PbMoO_4$ | $MoO_3$ | 0.3923 | 2.5491 |
| PbO | $PbCl_2$ | 1.2461 | 0.8025 |
| PbO | $PbCO_3$ | 1.1972 | 0.8353 |
| PbO | Pb | 0.9283 | 1.0772 |
| PbO | $PbCl_2$ | 1.2461 | 0.8025 |
| PbO | $PbCO_3$ | 1.1972 | 0.8353 |
| PbO | $Pb(NO_3)_2$ | 1.4842 | 0.6738 |
| PbO | $PbSO_4$ | 1.3589 | 0.7359 |
| PbS | Pb | 0.8659 | 1.1549 |
| PbS | PbO | 0.9328 | 1.0720 |
| PbS | S | 0.1341 | 7.4577 |
| $PbSO_4$ | $BaSO_4$ | 0.7700 | 1.2987 |
| $PbSO_4$ | $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ | 1.2507 | 0.7995 |
| $PbSO_4$ | $(PbCO_3)_2Pb(OH)_2$ | 0.8525 | 1.1731 |
| $PbSO_4$ | $PbO_2$ | 0.7887 | 1.2679 |
| $PbSO_4$ | $Pb_3O_4$ | 0.7535 | 1.3272 |
| $PbSO_4$ | PbS | 0.7889 | 1.2676 |
| Pd | $K_2PdCl_6$ | 3.7270 | 0.2683 |
| Pd | $PdCl_2 \cdot 2H_2O$ | 2.0024 | 0.4994 |
| Pd | $PdI_2$ | 3.3791 | 0.2959 |
| Pd | $Pd(NO_3)_2$ | 2.1623 | 0.4625 |
| Pd | HI | 2.3970 | 0.4170 |
| Pd | I | 2.3790 | 0.4203 |
| $PdI_2$ | HI | 0.7096 | 1.4092 |
| $PdI_2$ | I | 0.7040 | 1.4204 |
| Pt | $K_2PtCl_6$ | 2.4921 | 0.1609 |
| Pt | $H_2PtCl_6 \cdot 6H_2O$ | 2.6558 | 0.3765 |
| Pt | $(NH_4)_2PtCl_6$ | 2.2761 | 0.4393 |
| Pt | $PtCl_4$ | 1.7266 | 0.5792 |
| Pt | $PtCl_4 \cdot 5H_2O$ | 2.1881 | 0.4570 |
| $PtCl_4$ | $K_2PtCl_6$ | 1.4427 | 0.6931 |
| $PtCl_4$ | $(NH_4)_2PtCl_6$ | 1.3177 | 0.7589 |
| $PtCl_4 \cdot 5H_2O$ | $K_2PtCl_6$ | 1.1383 | 0.8785 |
| Pr | $Pr_2O_3$ | 1.1707 | 0.8542 |
| Rh | $Na_3RhCl_6$ | 3.7382 | 0.2675 |
| Rh | $RhCl_3$ | 2.0338 | 0.4917 |
| Rb | AgCl | 1.6775 | 0.5961 |
| Rb | Cl | 2.4098 | 0.4150 |
| Rb | RbCl | 1.4150 | 0.7067 |
| Rb | $RbCO_3$ | 1.3510 | 0.7402 |
| Rb | $Rb_2O$ | 1.0937 | 0.9144 |
| Rb | $Rb_2SO_4$ | 1.5622 | 0.6402 |
| Rb | $Rb_2PtCl_6$ | 3.3862 | 0.2952 |
| RbCl | AgCl | 1.8550 | 0.8435 |
| RbCl | Cl | 0.2933 | 3.4098 |
| $Rb_2CO_3$ | $RbHCO_3$ | 1.2686 | 0.7883 |
| $Rb_2O$ | RbCl | 1.2939 | 0.7729 |
| $Rb_2O$ | $Rb_2SO_4$ | 1.4284 | 0.7001 |
| $RbPtCl_6$ | RbCl | 0.4178 | 2.3938 |
| $RbPtCl_6$ | $Rb_2CO_3$ | 0.3987 | 2.5071 |
| $RbPtCl_6$ | $RbHCO_3$ | 0.5060 | 1.9762 |
| $RbPtCl_6$ | $Rb_2O$ | 0.3229 | 3.0972 |
| S | $BaSO_4$ | 7.2791 | 0.1374 |
| S | $H_2S$ | 1.0629 | 0.9388 |
| S | $H_2SO_4$ | 3.0585 | 0.3270 |
| S | FeS | 2.7412 | 0.3648 |
| S | $FeS_2$ | 1.8706 | 0.5346 |
| S | $Na_2S$ | 2.4344 | 0.4108 |
| S | Pb | 6.4599 | 0.1548 |

$A \times A' = B$ and $B \times B' = A$.

* Phenolphthalein.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ | A | B | A′ | B′ |
|---|---|---|---|---|---|---|---|
| S | $SO_2$ | 1.9978 | 0.5005 | $SiO_2$ | $K_2SiF_6$ | 3.6567 | 0.2735 |
| S | $SO_3$ | 2.4967 | 0.4005 | $SiO_2$ | $K_2SiO_3$ | 2.5622 | 0.3903 |
| $SO_2$ | $BaSO_4$ | 3.6430 | 0.2745 | $SiO_2$ | $SiF_4$ | 1.7296 | 0.5782 |
| $SO_2$ | $Ca(HSO_3)_2$ | 1.5783 | 0.6336 | $SiO_2$ | $SO_3$ | 0.7727 | 1.2942 |
| $SO_2$ | $H_2SO_3$ | 1.2812 | 0.7805 | $SiO_2$ | $Si(OH)_4$ | 1.5975 | 0.6259 |
| $SO_2$* | $H_2SO_4$ | 1.5309 | 0.6532 | $SiO_2$ | $ZnSiO_3$ | 2.3495 | 0.4256 |
| $SO_2$† | $H_2SO_4$ | 0.7655 | 1.3064 | | | | |
| $SO_2$ | $NaHSO_3$ | 1.6244 | 0.6156 | Sn | $Cl_2$ | 0.5975 | 1.6771 |
| $SO_2$ | $Na_2SO_3$ | 1.9677 | 0.5082 | Sn | $SnCl_2$ | 1.5974 | 0.6261 |
| $SO_2$ | $Na_2SO_3 \cdot 7H_2O$ | 3.9360 | 0.2541 | Sn | $SnCl_2 \cdot 2H_2O$ | 1.7325 | 0.5772 |
| $SO_3$ | $Al_2O_3$ | 0.4255 | 2.3504 | Sn | $SnCl_4$ | 2.1945 | 0.4555 |
| $SO_3$ | $Al_2(SO_4)_3$ | 1.4255 | 0.7015 | Sn | SnO | 1.1348 | 0.8812 |
| $SO_3$ | $BaSO_4$ | 2.9155 | 0.3430 | Sn | $SnO_2$ | 1.2696 | 0.7877 |
| $SO_3$ | CaO | 0.7003 | 1.4280 | $SnCl_2$ | Cl | 0.3740 | 2.6738 |
| $SO_3$ | $CaSO_4$ | 1.7003 | 0.5881 | $SnCl_2$ | HCl | 0.3847 | 2.6000 |
| $SO_3$ | $H_2SO_4$ | 1.2250 | 0.8163 | $SnCl_2$ | $Fe_2O_3$ | 1.0952 | 0.9130 |
| $SO_3$ | $K_2SO_4$ | 2.1765 | 0.4595 | $SnCl_2$ | $SnCl_2 \cdot 2H_2O$ | 1.0846 | 0.9221 |
| $SO_3$ | MgO(in $MgSO_4$) | 0.5036 | 1.9859 | $SnCl_4$ | Cl | 0.5444 | 1.8369 |
| | | | | $SnCl_4$ | HCl | 0.5568 | 1.7959 |
| $SO_3$ | $MgSO_4$ | 1.5036 | 0.6651 | $SnO_2$ | $SnCl_2 \cdot 2H_2O$ | 1.4974 | 0.6678 |
| $SO_3$ | $MnSO_4$ | 1.8858 | 0.5303 | $SnO_2$ | $SnCl_4$ | 1.7288 | 0.5784 |
| $SO_3$ | $Na_2O$ | 0.7743 | 1.2915 | $SnO_2$ | $SnCl_4$ $(NH_4Cl)_2$ | 2.4389 | 0.4100 |
| $SO_3$ | $Na_2SO_4$ | 1.7743 | 0.5636 | | | | |
| $SO_3$ | 66° O. V. | 1.3146 | 0.7607 | $SnO_2$ | SnO | 0.8938 | 1.1188 |
| $SO_3$ | $ZnSO_4$ | 2.0162 | 0.4960 | | | | |
| $SO_4$ | $BaSO_4$ | 2.4298 | 0.4116 | Sr | $SrCO_3$ | 1.6848 | 0.5935 |
| $SO_3 \cdot HCl$ | $H_2SO_4$ | 1.2625 | 0.7921 | Sr | SrO | 1.1826 | 0.8456 |
| $S_2O_5Cl_2$ | $H_2SO_4$ | 1.3683 | 0.7309 | Sr | $SrSO_4$ | 2.0963 | 0.4770 |
| | | | | SrO | $SrCl_2$ | 1.5300 | 0.6536 |
| Sb | $KSbOC_4H_4O_6 \cdot \frac{1}{2}H_2O$ | 2.7649 | 0.3617 | $SrSO_4$ | $SO_3$ | 0.4357 | 2.2943 |
| Sb | $SbCl_3$ | 1.8850 | 0.5305 | Ta | $TaCl_5$ | 1.9767 | 0.5059 |
| Sb | $Sb_2O_3$ | 1.1997 | 0.8336 | Ta | $Ta_2O_5$ | 1.2162 | 0.8207 |
| Sb | $Sb_2O_5$ | 1.3328 | 0.7503 | | | | |
| Sb | $Sb_2S_3$ | 1.4002 | 0.7142 | Te | $H_2TeO_4$ | 1.5177 | 0.6587 |
| Sb | $Sb_2O_4$ | 1.2662 | 0.7897 | Te | $H_2TeO_4 2H_2O$ | 1.8003 | 0.5554 |
| $Sb_2O_3$ | $Sb_2O_5$ | 1.1109 | 0.9001 | Te | $TeO_2$ | 1.2509 | 0.7994 |
| $Sb_2S_3$ | $SbCl_3$ | 1.3462 | 0.7428 | Te | $TeO_3$ | 1.3765 | 0.7265 |
| Se | $H_2SeO_3$ | 1.6315 | 0 6129 | $ThO_2$ | Th | 0.8790 | 1.1379 |
| Se | $H_2SeO_4$ | 1.8336 | 0.5454 | $ThO_2$ | $ThCl_4$ | 1.4155 | 0.7065 |
| Se | $SeO_2$ | 1.4040 | 0.7123 | $ThO_2$ | $Th(NO_3)_4 \cdot 6H_2O$ | 2.2226 | 0.4492 |
| Se | $SeO_3$ | 1.6060 | 0.6227 | | | | |
| Si | $SiO_2$ | 2.1307 | 0.4693 | Ti | $TiO_2$ | 1.6652 | 0.6005 |
| Si | $SiO_3$ | 1.2653 | 0.7903 | | | | |
| Si | $SiO_4$ | 1.5307 | 0.6533 | Tl | TlCl | 1.1738 | 0.8519 |
| $SiF_4$ | $BaSiF_6$ | 2.6814 | 0.3729 | Tl | $Tl_2CO_3$ | 1.1470 | 0.8718 |
| $SiF_4$ | $H_2SiF_6$ | 1.3837 | 0.7227 | Tl | TlI | 1.622 | 0.6165 |
| $SiF_4$ | $K_2SiF_6$ | 2.1141 | 0.4730 | Tl | $TlNO_3$ | 1.3040 | 0.7669 |
| $SiF_6$ | $H_2SiF_6$ | 1.0141 | 0.9860 | Tl | $Tl_2O$ | 1.0392 | 0.9623 |
| $SiO_2$ | $BaSiF_6$ | 4.6380 | 0.2156 | $Tl_2CrO_4$ | Tl | 0.7786 | 1.2843 |
| $SiO_2$ | $H_2SiO_3$ | 1.2988 | 0.7699 | $TlHSO_4$ | Tl | 0.6775 | 1.4759 |

$A \times A' = B$ and $B \times B' = A$.

* Phenolphthalein. † Methyl Orange.

## TABLES AND USEFUL DATA

### VIII.—CONVERSION FACTORS (Continued)

| A | B | A′ | B′ | A | B | A′ | B′ |
|---|---|---|---|---|---|---|---|
| TlI | Tl | 0.6165 | 1.6222 | $WO_3$ | W | 0.7931 | 1.2609 |
| $Tl_2PtCl_6$ | Tl | 0.5000 | 1.9999 | $WO_3$ | $PbWO_4$ | 1.9610 | 0.5099 |
| $Tl_2PtCl_6$ | TlCl | 0.5869 | 1.7038 | | | | |
| $Tl_2PtCl_6$ | $Tl_2CO_3$ | 0.5738 | 1.7435 | Zn | $H_2SO_4$ | 1.5004 | 0.6665 |
| $Tl_2PtCl_6$ | TlI | 0.8111 | 1.2329 | Zn | $SO_3$ | 1.4229 | 0.8164 |
| $Tl_2PtCl_6$ | $TlNO_3$ | 0.6520 | 1.5337 | Zn | $ZnCl_2$ | 2.0849 | 0.4796 |
| $Tl_2PtCl_6$ | $Tl_2O$ | 0.5196 | 1.9244 | Zn | ZnO | 1.2448 | 0.8034 |
| $Tl_2PtCl_6$ | $Tl_2SO_4$ | 0.6178 | 1.6187 | Zn | $ZnP_2O_7$ | 2.3309 | 0.4290 |
| $Tl_2SO_4$ | Tl | 0.8094 | 1.6187 | Zn | ZnS | 1.4906 | 0.6709 |
| | | | | $ZnCl_2$ | AgCl | 2.1035 | 0.4754 |
| $UO_2$ | U | 0.8817 | 1.1342 | $ZnCl_2$ | Cl | 0.5204 | 1.9217 |
| $U_3O_8$ | U | 0.8482 | 1.1789 | $ZnCl_2$ | NaCl | 0.8579 | 1.1656 |
| $U_3O_8$ | $UO_2$ | 0.9621 | 1.0394 | ZnO | $H_2SO_4$ | 1.2054 | 0.8296 |
| $U_3O_8$ | $UO_2(NO_3)_2$ ·$6H_2O$ | 1.7876 | 0.5594 | ZnO | $SO_3$ | 0.9840 | 1.0162 |
| | | | | ZnO | $ZnCl_2$ | 1.6749 | 0.5970 |
| $U_2P_2O_{11}$ | U | 0.6671 | 1.4990 | ZnO | $ZnCO_3$ | 1.5407 | 0.6490 |
| $U_2P_2O_{11}$ | $UO_2$ | 0.7566 | 1.3216 | ZnO | $ZnP_2O_7$ | 1.8726 | 0.5340 |
| | | | | ZnO | ZnS | 1.1975 | 0.8351 |
| $V_2O_4$ | V | 0.6024 | 1.6276 | ZnO | $ZnSO_4$ | 1.9840 | 0.5040 |
| $V_2O_5$ | V | 0.5604 | 1.7843 | ZnO | $ZnSO_4 \cdot 7H_2O$ | 3.5340 | 0.2830 |
| $V_2O_5$ | $VO_4$ | 1.2638 | 0.7913 | ZnS | $BaSO_4$ | 2.3957 | 0.4174 |
| | | | | ZnS | $ZnSO_4 \cdot 7H_2O$ | 2.9510 | 0.3389 |
| $Yb_2O_3$ | Yb | 0.8775 | 1.1396 | $ZnSiO_3$ | $SiO_2$ | 0.4250 | 2.3495 |
| $Y_2O_3$ | Y | 0.7876 | 1.2697 | $ZnSO_4$ | $SO_3$ | 0.4960 | 2.0162 |
| W | $PbWO_4$ | 3.4477 | 0.2900 | $ZrO_2$ | Zr | 0.7390 | 1.3532 |
| $WO_2$ | W | 0.8519 | 1.1739 | | | | |

$A \times A' = B$ and $B \times B' = A$.

NOTE.—The editor will welcome additional factors not appearing in these tables. A number of factors appearing in this list were taken from Van Nostrand's Chemical Annual. Olsen. 1913.

*Example of Method for Using Factors.* Suppose the product weighed is 0.8535 gram AgCl and the equivalent weight of Cl is desired; hunt up the factors AgCl–Cl. This may be found on the first page of the conversion factors, a little below the middle of the page. Using the formula $A \times A' = B$, and substituting the values for $A$ (weight of AgCl) and $A'$ (factor) we have $0.8535 \times 0.2474 = 0.21124$ gram Cl. If on the other hand, the weight of Cl were known to be, say, 0.2501 gram and the weight of the equivalent AgCl were desired, we would use the formula $B \times B' = A$ and, substituting the values for $B$ and $B'$, we would have $0.2501 \times 4.0423 = 1.01098$ gram AgCl.

### VOLUMETRIC FACTORS

1 cc. N/2 HCl = .018185 gram HCl.
1 cc. N/10HCl = .003637 gram HCl.
1 cc. N/2 KOH = .028 gram KOH.
1 cc. N/6 KOH = .047 gram oleic acid = .008133 gram $H_2SO_4$.
1 cc. N/10 KOH = .0056 gram KOH.
1 cc. $K_2Cr_2O_7$ 3.8633 gram per liter = .0038633 gram $K_2Cr_2O_7$ = .010 gram I.
1 cc. N/10 $Na_2S_2O_3 + 5H_2O$ = .0248 gram $Na_2S_2O_3 + 5H_2O$ = .01265 gram I.

## TABLES AND USEFUL DATA

### IX.—COMPARISON OF CENTIGRADE AND FAHRENHEIT SCALE

| °C. | −100 | −0 | +0 | +100 | +200 | +300 | +400 | +500 | +600 | +700 | +800 | +900 | °C. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | °F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | |
| 0 | −148 | + 32 | 32 | +212 | 392 | 572 | 752 | 932 | 1112 | 1292 | 1472 | 1652 | 0 |
| 5 | −157 | + 23 | 41 | 221 | 401 | 581 | 761 | 941 | 1121 | 1301 | 1481 | 1661 | 5 |
| 10 | −166 | + 14 | 50 | 230 | 410 | 590 | 770 | 950 | 1130 | 1310 | 1490 | 1670 | 10 |
| 15 | −175 | + 5 | 59 | 239 | 419 | 599 | 779 | 959 | 1139 | 1319 | 1499 | 1679 | 15 |
| 20 | −184 | − 4 | 68 | 248 | 428 | 608 | 788 | 968 | 1148 | 1328 | 1508 | 1688 | 20 |
| 25 | −193 | − 13 | 77 | 257 | 437 | 617 | 797 | 977 | 1157 | 1337 | 1517 | 1697 | 25 |
| 30 | −202 | − 22 | 86 | 266 | 446 | 626 | 806 | 986 | 1166 | 1346 | 1526 | 1706 | 30 |
| 35 | −211 | − 31 | 95 | 275 | 455 | 635 | 815 | 995 | 1175 | 1355 | 1535 | 1715 | 35 |
| 40 | −220 | − 40 | 104 | 284 | 464 | 644 | 824 | 1004 | 1184 | 1364 | 1544 | 1724 | 40 |
| 45 | −229 | − 49 | 113 | 293 | 473 | 653 | 833 | 1013 | 1193 | 1373 | 1553 | 1733 | 45 |
| 50 | −238 | − 58 | 122 | 302 | 482 | 662 | 842 | 1022 | 1202 | 1382 | 1562 | 1742 | 50 |
| 55 | −247 | − 67 | 131 | 311 | 491 | 671 | 851 | 1031 | 1211 | 1391 | 1571 | 1751 | 55 |
| 60 | −256 | − 76 | 140 | 320 | 500 | 680 | 860 | 1040 | 1220 | 1400 | 1580 | 1760 | 60 |
| 65 | −265 | − 85 | 149 | 329 | 509 | 689 | 869 | 1049 | 1229 | 1409 | 1589 | 1769 | 65 |
| 70 | −274 | − 94 | 158 | 338 | 518 | 698 | 878 | 1058 | 1238 | 1418 | 1598 | 1778 | 70 |
| 75 | −283 | −103 | 167 | 347 | 527 | 707 | 887 | 1067 | 1247 | 1427 | 1607 | 1787 | 75 |
| 80 | −292 | −112 | 176 | 356 | 536 | 716 | 896 | 1076 | 1256 | 1436 | 1616 | 1796 | 80 |
| 85 | −301 | −121 | 185 | 365 | 545 | 725 | 905 | 1085 | 1265 | 1445 | 1625 | 1805 | 85 |
| 90 | −310 | −130 | 194 | 374 | 554 | 734 | 914 | 1094 | 1274 | 1454 | 1634 | 1814 | 90 |
| 95 | −319 | −139 | 203 | 383 | 563 | 743 | 923 | 1103 | 1283 | 1463 | 1643 | 1823 | 95 |
| 100 | −328 | −148 | +212 | 392 | 572 | 752 | 932 | 1112 | 1292 | 1472 | 1652 | 1832 | 100 |

| °C. | −200 | −100 | +100 | +200 | +300 | +400 | +500 | +600 | +700 | +800 | +900 | +1000 | °C. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| C° | 1100 | 1200 | 1300 | 1400 | 1500 | 1600 | 1700 | 1800 | 1900 | 2000 |
| F° | 2012 | 2192 | 2372 | 2552 | 2732 | 2912 | 3092 | 3272 | 3452 | 3632 |

Degrees C. × 1.8 + 32 = Degrees F. Degrees F. − 32 ÷ 1.8 = Degrees C.

Absolute zero, −273° C. = −459° F.

### Comparison of Centigrade and Fahrenheit Scale for Every 1° C. from 0° to 100° C.

| C. | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | C. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | |
| 0 | 32 | 50 | 68 | 86 | 104 | 122 | 140 | 158 | 176 | 194 | 0 |
| 1 | 33.8 | 51.8 | 69.8 | 87.8 | 105.8 | 123.8 | 141.8 | 159.8 | 177.8 | 195.8 | 1 |
| 2 | 35.6 | 53.6 | 71.6 | 89.6 | 107.6 | 125.6 | 143.6 | 161.6 | 179.6 | 197.6 | 2 |
| 3 | 37.4 | 55.4 | 73.4 | 91.4 | 109.4 | 127.4 | 145.4 | 163.4 | 181.4 | 199.4 | 3 |
| 4 | 39.2 | 57.2 | 75.2 | 93.2 | 111.2 | 129.2 | 147.2 | 165.2 | 183.2 | 201.2 | 4 |
| 5 | 41.0 | 59 | 77 | 95 | 113 | 131 | 149 | 167 | 185 | 203 | 5 |
| 6 | 42.8 | 60.8 | 78.8 | 96.8 | 114.8 | 132.8 | 150.8 | 168.8 | 186.8 | 204.8 | 6 |
| 7 | 44.6 | 62.6 | 80.6 | 98.6 | 116.6 | 134.6 | 152.6 | 170.6 | 188.6 | 206.6 | 7 |
| 8 | 46.4 | 64.4 | 82.4 | 100.4 | 118.4 | 136.4 | 154.4 | 172.4 | 190.4 | 208.4 | 8 |
| 9 | 48.2 | 66.2 | 84.2 | 102.2 | 120.2 | 138.2 | 156.2 | 174.2 | 192.2 | 210.2 | 9 |

| C. | 9 | 19 | 29 | 39 | 49 | 59 | 69 | 79 | 89 | 99 | C. |
|---|---|---|---|---|---|---|---|---|---|---|---|

100° C. = 212° F.

## TABLES AND USEFUL DATA

### X.—RELATION OF BAUMÉ DEGREES TO SPECIFIC GRAVITY AND THE WEIGHT OF ONE UNITED STATES GALLON AT 60° F.—LIQUIDS LIGHTER THAN WATER

| Baumé. | Specific Gravity. | Pounds in Gallon. | Baumé. | Specific Gravity. | Pounds in Gallon. | Baumé. | Specific Gravity. | Pounds in Gallon. | Baumé. | Specific Gravity. | Pounds in Gallon. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | 1.0000 | 8.33 | 31 | 0.8695 | 7.24 | 52 | 0.7692 | 6.41 | 73 | 0.6896 | 5.75 |
| 11 | 0.9929 | 8.27 | 32 | 0.8641 | 7.20 | 53 | 0.7650 | 6.37 | 74 | 0.6863 | 5.52 |
| 12 | 0.9859 | 8.21 | 33 | 0.8588 | 7.15 | 54 | 0.7608 | 6.34 | 75 | 0.6829 | 5.69 |
| 13 | 0.9790 | 8.16 | 34 | 0.8536 | 7.11 | 55 | 0.7567 | 6.30 | 76 | 0.6796 | 5.66 |
| 14 | 0.9722 | 8.10 | 35 | 0.8484 | 7.07 | 56 | 0.7526 | 6.27 | 77 | 0.6763 | 5.63 |
| 15 | 0.9655 | 8.04 | 36 | 0.8433 | 7.03 | 57 | 0.7486 | 6.24 | 78 | 0.6730 | 5.60 |
| 16 | 0.9589 | 7.99 | 37 | 0.8383 | 6.98 | 58 | 0.7446 | 6.20 | 79 | 0.6698 | 5.58 |
| 17 | 0.9523 | 7.93 | 38 | 0.8333 | 6.94 | 59 | 0.7407 | 6.17 | 80 | 0.6666 | 5.55 |
| 18 | 0.9459 | 7.88 | 39 | 0.8284 | 6.90 | 60 | 0.7368 | 6.14 | 81 | 0.6635 | 5.52 |
| 19 | 0.9395 | 7.83 | 40 | 0.8235 | 6.86 | 61 | 0.7329 | 6.11 | 82 | 0.6604 | 5.50 |
| 20 | 0.9333 | 7.78 | 41 | 0.8187 | 6.82 | 62 | 0.7290 | 6.07 | 83 | 0.6573 | 5.48 |
| 21 | 0.9271 | 7.72 | 42 | 0.8139 | 6.78 | 63 | 0.7253 | 6.04 | 84 | 0.6542 | 5.45 |
| 22 | 0.9210 | 7.67 | 43 | 0.8092 | 6.74 | 64 | 0.7216 | 6.01 | 85 | 0.6511 | 5.42 |
| 23 | 0.9150 | 7.62 | 44 | 0.8045 | 6.70 | 65 | 0.7179 | 5.98 | 86 | 0.6481 | 5.40 |
| 24 | 0.9090 | 7.57 | 45 | 0.8000 | 6.66 | 66 | 0.7142 | 5.95 | 87 | 0.6451 | 5.38 |
| 25 | 0.9032 | 7.53 | 46 | 0.7954 | 6.63 | 67 | 0.7106 | 5.92 | 88 | 0.6422 | 5.36 |
| 26 | 0.8974 | 7.48 | 47 | 0.7909 | 6.59 | 68 | 0.7070 | 5.89 | 89 | 0.6392 | 5.33 |
| 27 | 0.8917 | 7.43 | 48 | 0.7865 | 6.55 | 69 | 0.7035 | 5.86 | 90 | 0.6363 | 5.30 |
| 28 | 0.8860 | 7.38 | 49 | 0.7821 | 6.52 | 70 | 0.7000 | 5.83 | 95 | 0.6222 | 5.18 |
| 29 | 0.8805 | 7.34 | 50 | 0.7777 | 6.43 | 71 | 0.6965 | 5.80 | .. | ..... | ... |
| 30 | 0.8750 | 7.29 | 51 | 0.7734 | 6.44 | 72 | 0.6930 | 5.78 | .. | ..... | ... |

### X.—(*a*) RELATION OF BAUMÉ DEGREES TO, SPECIFIC GRAVITY—LIQUIDS HEAVIER THAN WATER

| Baumé Degrees. | Specific Gravity. | Baumé Degrees. | Specific Gravity. | Baumé Degrees. | Specific Gravity. | Baumé Degrees. | Specific Gravity. |
|---|---|---|---|---|---|---|---|
| 0.0 | 1.0000 | 6.0 | 1.0432 | 24.0 | 1.1983 | 42.0 | 1.4078 |
| 0.1 | 1.0007 | 7.0 | 1.0507 | 25.0 | 1.2083 | 43.0 | 1.4216 |
| 0.2 | 1.0014 | 8.0 | 1.0584 | 26.0 | 1.2185 | 44.0 | 1.4356 |
| 0.3 | 1.0021 | 9.0 | 1.0662 | 27.0 | 1.2288 | 45.0 | 1.4500 |
| 0.4 | 1.0028 | 10.0 | 1.0741 | 28.0 | 1.2393 | 46.0 | 1.4646 |
| 0.5 | 1.0035 | 11.0 | 1.0821 | 29.0 | 1.2500 | 47.0 | 1.4796 |
| 0.6 | 1.0042 | 12.0 | 1.0902 | 30.0 | 1.2609 | 48.0 | 1.4948 |
| 0.7 | 1.0049 | 13.0 | 1.0985 | 31.0 | 1.2719 | 49.0 | 1.5104 |
| 0.8 | 1.0055 | 14.0 | 1.1069 | 32.0 | 1.2832 | 50.0 | 1.5263 |
| 0.9 | 1.0062 | 15.0 | 1.1154 | 33.0 | 1.2946 | 51.0 | 1.5426 |
| 1.0 | 1.0069 | 16.0 | 1.1240 | 34.0 | 1.3063 | 52.0 | 1.5591 |
| 1.5 | 1.0105 | 17.0 | 1.1328 | 35.0 | 1.3282 | 53.0 | 1.5761 |
| 2.0 | 1.0140 | 18.0 | 1.1417 | 36.0 | 1.3303 | 54.0 | 1.5934 |
| 2.5 | 1.0175 | 19.0 | 1.1508 | 37.0 | 1.3426 | 55.0 | 1.6111 |
| 3.0 | 1.0211 | 20.0 | 1.1600 | 38.0 | 1.3551 | 56.0 | 1.6292 |
| 3.5 | 1.0247 | 21.0 | 1.1694 | 39.0 | 1.3679 | 57.0 | 1.6477 |
| 4.0 | 1.0284 | 22.0 | 1.1789 | 40.0 | 1.3810 | 58.0 | 1.6667 |
| 5.0 | 1.0357 | 23.0 | 1.1885 | 41.0 | 1.3942 | 59.0 | 1.6860 |
| | | | | | | 60.0 | 1.7059 |

# TABLES AND USEFUL DATA

## XI.—COMPARISON OF METRIC AND CUSTOMARY UNITS (U. S.).

### Length

| | | | |
|---|---|---|---|
| 1 millimeter, mm. | =0.03937 inch. | 1 inch | =25.4001 millimeters. |
| 1 centimeter, cm. | =0.39371 inch. | 1 inch | = 2.54001 centimeters. |
| 1 meter, m. | =3.28083 feet. | 1 foot | = 0.304801 meter. |
| 1 meter | =1.09361 yards. | 1 yard | = 0.914402 meter. |
| 1 kilometer | =0.62137 (U. S.) mile. | 1 mile | = 1.60935 kilometers. |

### Areas

| | | | |
|---|---|---|---|
| 1 square millimeter, sq.mm. | = 0.00155 sq.in. | 1 sq.in. | =645.16 sq.mm. |
| 1 square centimeter, sq.cm. | = 0.1550 sq.in. | 1 sq.in. | = 6.452 sq.cm. |
| 1 square meter, sq.m. | =10.764 sq.ft. | 1 sq.ft. | = 0.0929 sq.m. |
| 1 square meter | = 1.196 sq.yd. | 1 sq.yd. | = 0.8361 sq.m. |
| 1 square kilometers | = 0.3861 sq.mi. | 1 sq.mi. | = 2.5900 sq.km. |
| 1 hectare | = 2.471 acres. | 1 acre | = 0.4047 hectare |

### Volumes

| | | | |
|---|---|---|---|
| 1 cubic millimeter, cu.mm. | = 0.000061 in. | 1 cu.in. | =16,387.2 cu.mm. |
| 1 cubic centimeter, cc. | = 0.06103 cu.in. | 1 cu.in. | =16.3872 cc. |
| 1 cubic meter | =35.314 cu.ft. | 1 cu.ft. | = 0.02832 cu.m. |
| | =61,028 cu.ins. | | =28.32 liters. |
| 1 cubic meter | = 1.3079 cu.yd. | 1 cu.yd. | = 0.7645 cu.m |

### Capacities

| | | | |
|---|---|---|---|
| 1 cubic centimeter, cc. | =0.03381 (U.S.) liquid ounce. | 1 ounce | =29.574 cc. |
| 1 cubic centimeter | =0.2705 (U. S.) apothecaries' dram. | 1 dram | =3.6967 cc. |
| 1 cubic centimeter | =0.8115 (U. S.) apothecaries' scruple. | 1 scruple | =1.2322 cc. |
| 1 liter | =1.05668 (U. S.) liquid quarts. | 1 quart | =0.94636 liter. |
| 1 liter | =0.26417 (U. S.) gallon. | 1 gallon | =3.78543 liters. |
| 1 liter | =0.11351 (U. S.) peck. | 1 peck | =8.80982 liters. |
| 1 hectoliter | =2.83774 (U. S.) bushels. | 1 bushel | =0.35239 hectoliter. |

### Masses

| | | | |
|---|---|---|---|
| 1 gram | =15.4324 grains. | 1 grain | = 0.06480 gram. |
| 1 gram | = 0.03527 avoirdupois ounce. | 1 ounce (av.) | =28.3495 grams. |
| 1 gram | = 0.03215 troy ounce. | 1 ounce (troy) | =31.10348 grams. |
| 1 kilogram | = 2.20462 pounds (av.) | 1 pound (av.) | = 0.45359 kilogram. |
| 1 kilogram | = 2.67923 pounds (troy). | 1 pound (troy) | = 0.37324 kilogram. |

Table of Equivalents, U. S. Bureau of Standards. For British Imperial Weights and Measures see Van Nostrand's Chemical Annual.

### Avoirdupois Weight

The system of weights in ordinary use by which common or heavy articles are weighed.

| | | |
|---|---|---|
| 16 drams | =1 ounce | = 28.35 grams. |
| 16 ounces | =1 pound | =453.59 grams. |
| 25 pounds | =1 quarter | = 11.34 kilograms. |
| 4 quarters | =1 hundred weight | = 45.359 kilograms. |

1 avoirdupois pound contains 7000 grains.

1 avoirdupois ounce contains 437.5 grains.

## TABLES AND USEFUL DATA

### Apothecaries' Weight

The system of weights employed in weighing medicines.

| | | |
|---|---|---|
| 1 grain | = | 0.0648 gram. |
| 20 grains | = 1 scruple = | 1.296 grams. |
| 3 scruples | = 1 drachm = | 3.888 grams. |
| 8 drachms | = 1 ounce = | 31.103 grams. |
| 12 ounces | = 1 pound = | 373.236 grams. |

1 apothecaries' (or troy) pound contains 5760 grains.
1 apothecaries' (or troy) ounce contains 480 grains.

### Fluid Measure

| | | | |
|---|---|---|---|
| 1 minim | = | .06161 | cubic centimeter. |
| 60 minims | = 1 fluid drachm = | 3.696 | cubic centimeters. |
| 8 fluid drachms | = 1 fluid ounce = | 29.573 | cubic centimeters. |
| 16 fluid ounces | = 1 pint = | 473.179 | cubic centimeters. |
| 8 pints | = 1 gallon = | 3.785 | liters. |

1 gallon contains 231 cubic inches.

The minim, fluid drachm, fluid ounce and pint are the fluid measures employed by apothecaries.

### XII.—INTER-CONVERSION TABLE

| To Convert From | Multiply by | | | | |
|---|---|---|---|---|---|
| | Lbs. per Sq. In. | Tons per Sq. In. | Kg. per Sq. Cm. | M. Tons per Sq. Cm. | Atmospheres |
| Lbs. per Sq. In.... | 1.00000 | .000446 | .070307 | .$0_4$7031 | .068041 |
| Tons per Sq. In.... | 2240.00 | 1.00000 | 157.488 | .157488 | 152.412 |
| Kg. per Sq. Cm.... | 14.2233 | .006350 | 1.00000 | .001000 | .967768 |
| Metric Tons per Sq. Cm..... | 14223.0 | 6.34969 | 1000.00 | 1.00000 | 967.768 |
| Atmospheres..... | 14.6970 | .006558 | 1.03329 | .001033 | 1.00000 |

1 gram = 15.43 grains
1 gram = .0468 grams
1 m. = 3.28 ft.

The above tables were obtained by courtesy of Du Pont de Nemours Company through the kindness of Dr. E. C. Lathrop.

## XIII.—ENERGY CONVERSION FACTORS

| To Convert From | Multiply by | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | B. T. U. | P. C. U. | Cal. | Ft. Lbs. | Ft. Tons | Kg. M. | HP Hrs. | KW Hrs. | Joules | Lbs. C | Lbs. $H_2O$ |
| B. T. U. | 1.00000 | .555556 | .251996 | 778.000 | .389001 | 107.563 | $.0_33929$ | $.0_32931$ | 1055.20 | $.0_46876$ | .001031 |
| P. C. U. | 1.80000 | 1.00000 | .453593 | 1400.40 | .700202 | 193.613 | $.0_37072$ | $.0_35276$ | 1899.36 | $.0_31238$ | .001855 |
| Calories | 3.96832 | 2.20462 | 1.00000 | 3091.36 | 1.54368 | 426.844 | .001559 | .001163 | 4187.37 | $.0_32729$ | .004089 |
| Ft. Lbs. | .001285 | $.0_37141$ | $.0_33239$ | 1.00000 | .000500 | .138255 | $.0_65050$ | $.0_63767$ | 1.35625 | $.0_78840$ | $.0_31325$ |
| Fr. Tons | 2.57069 | 1.42816 | .647804 | 2000.00 | 1.00000 | 276.511 | .001010 | $.0_37535$ | 2712.59 | $.0_31768$ | .002649 |
| Kg. M. | .009297 | 005165 | .002343 | 7.23301 | .003617 | 1.00000 | $.0_33653$ | $.0_32725$ | 9.81069 | $.0_66394$ | $.0_39580$ |
| HP Hrs. | 2544.99 | .141388 | 641.327 | 1980000 | 990.004 | 273747 | 1.00000 | .746000 | 2685473 | .175044 | 2.62261 |
| KW Hrs. | 3411.57 | 1895.32 | 859.702 | 2654200 | 1327.10 | 366959 | 1.34041 | 1.00000 | 3599889 | .234648 | 3.51562 |
| Joules | $.0_39477$ | $.0_35265$ | $.0_32388$ | .737311 | $.0_33687$ | .101937 | $.0_63724$ | $.0_42778$ | 1.00000 | $.0_76518$ | $.0_69766$ |
| Lbs. C. | 14544.0 | 8080.00 | 3665.03 | $113150_3$ | 5657.63 | 1564396 | 5.71434 | 4.26285 | $153470_3$ | 1.00000 | 14.9876 |
| Lbs. $H_2O$ | 970.400 | 539.111 | 244.537 | 754971 | 377.487 | 104379 | .381270 | .284424 | 1023966 | .066744 | 1.00000 |

"P. C. U." refers to the "pound-centigrade unit." The ton used is 2000 pounds. "Lbs. C" refers to pounds of carbon oxidized, 100 % efficiency, equivalent to the corresponding number of heat units. "Lbs. $H_2O$" refers to pounds of water evaporated at 100° C. = 212° F. at 100% efficiency. The sub-numeral following a zero indicates that the zero should be taken the number of times indicated. Thus: $0_33653$ is equivalent to .000003653.

## INTER-CONVERSION TABLE

| To Convert from | Multiply by | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Grains per Cu. Ft. | Ounces per Cu. Ft. | Pounds per Cu. Ft. | Grams per Cu. Ft. | Grains per Gallon | Ounces per Gallon | Pounds per Gallon | Grains per Cu. In. | Ounces per Cu. In. | Grams per Liter |
| Grains per Cu. Ft. | 1.00000 | .002286 | $.0_31428$ | .064799 | .133680 | $.0_33056$ | $.0_41910$ | $.0_35787$ | $.0_31323$ | .002288 |
| Oz. per Cu. Ft. | 437.500 | 1.00000 | .062497 | 28.4954 | 58.4848 | .133678 | .008355 | .253180 | $.0_35786$ | 1.00103 |
| Lbs. per Cu. Ft. | 7000.00 | 16.0000 | 1.00000 | 453.593 | 935.757 | 2.13885 | .133680 | 4.05090 | .009258 | 16.0163 |
| G. per Cu. Ft. | 15.4324 | .035274 | .002205 | 1.00000 | 2.06302 | .004715 | $.0_32947$ | .008931 | $.0_42041$ | .035310 |
| Grains per Gallon | 7.48050 | .017098 | .001069 | .484727 | 1.00000 | .002286 | $.0_31428$ | .004329 | $.0_39894$ | .017116 |
| Oz. per Gallon | 3272.72 | 7.48050 | .467510 | 21.2068 | 437.500 | 1.00000 | .062499 | 1.89392 | .003429 | 7.48798 |
| Lbs. per Gallon | 52363.6 | 119.690 | 7.48014 | 3393.09 | 7000.00 | 16.0000 | 1.00000 | 30.3028 | .069261 | 119.808 |
| Grains per Cu. In. | 1728.00 | 3.94960 | .246840 | 111.972 | 231.000 | .527990 | .032990 | 1.00000 | .002285 | 3.95380 |
| Oz. per Cu. In. | 756000 | 1728.00 | 108.000 | 48987.8 | 101061 | 231.000 | 14.4370 | 437.500 | 1.00000 | 1729.73 |
| G. per Liter | 437.050 | .998950 | .062432 | 28.3203 | 58.4220 | .133540 | .008346 | .252910 | $.0_35780$ | 1.00000 |

## XIV.—VOLUME AND WEIGHT CONVERSION TABLE

| To Convert From | Multiply by | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | To Cu. In. | To Cu. Ft. | To Cu. Yd. | To Fl. Oz. | To Pint. | To Quart. | To Gallon. | To Grain. | To Oz. Troy. | To Oz. Av. | To Lb. Troy. | To Lb. Av. | To CC. or G. | To Ltr. or Kg. | To Cu. M. |
| Cu. In. | 1.00000 | $.0_357S7$ | $.0_42143$ | .554112 | .034632 | .017316 | .004329 | 252.891 | .526857 | .578037 | .043905 | .036127 | 16.3871 | .016387 | $.0_41639$ |
| Cu. Ft. | 1728.00 | 1.00000 | .037037 | 957.505 | 59.8442 | 29.9221 | 7.48052 | 436996 | 910.408 | 998.848 | 75.8674 | 62.4280 | 28316.9 | 28.3169 | .028317 |
| Cu. Yd. | 46656.0 | 27.0000 | 1.00000 | 25852.6 | 1615.79 | 807.896 | 201.974 | $117990_3$ | 24581.0 | 26968.9 | 2048.42 | 1685.56 | 764556 | 764.556 | .764556 |
| Fl. Oz. | 1.80469 | .001044 | $.0_43868$ | 1.00000 | .062500 | .031520 | .007813 | 456.390 | .950813 | 1.04318 | .079234 | .065199 | 29.5736 | .029573 | $.0_42957$ |
| Pint | 28.8750 | .016710 | $.0_36189$ | 16.0000 | 1.00000 | .500000 | .125000 | 7302.23 | 15.2130 | 16.6908 | 1.26775 | 1.04318 | 473.177 | .473177 | $.0_44732$ |
| Quart | 57.7500 | .033420 | .001238 | 32.0000 | 2.00000 | 1.00000 | .250000 | 1460.45 | 30.4260 | 33.3816 | 2.53550 | 2.08635 | 946.354 | .946354 | $.0_39463$ |
| Gallon | 231.000 | .133681 | .004951 | 128.000 | 8.00000 | 4.00000 | 1.00000 | 58417.9 | 121.704 | 133.527 | 10.1420 | 8.34541 | 3785.42 | 3.78542 | .003785 |
| Grain | .003954 | $.0_52288$ | $.0_78475$ | .002191 | $.0_31369$ | $.0_46850$ | $.0_41712$ | 1.00000 | .002083 | .002286 | $.0_31736$ | $.0_31428$ | .064799 | $.0_46479$ | $.0_76479$ |
| Oz. Troy | 1.89805 | .001098 | $.0_44068$ | 1.05173 | .065733 | .032867 | .008217 | 480.000 | 1.00000 | 1.09714 | .083333 | .068571 | 31.1035 | .031104 | $.0_43110$ |
| Oz. Av. | 1.72999 | .001001 | $.0_43708$ | .958608 | .059913 | .029957 | .007489 | 437.500 | .911457 | 1.00000 | .075955 | .062500 | 28.3495 | .028350 | $.0_42835$ |
| Lb. Troy | 22.7766 | .013181 | $.0_34882$ | 12.6208 | .788800 | .394400 | .098600 | 5760.00 | 12.0000 | 13.1657 | 1.00000 | .822857 | 373.242 | .373242 | $.0_33732$ |
| Lb. Av. | 27.6799 | .016018 | $.0_35933$ | 15.3378 | .958611 | .479306 | .119826 | 70000.0 | 14.5833 | 16.0000 | 1.21528 | 1.00000 | 453.593 | .453593 | $.0_34536$ |
| CC or Gram | .061024 | $.0_43531$ | $.0_31308$ | .033814 | .002113 | .001057 | $.0_32642$ | 15.4323 | .032151 | .035274 | .002679 | .002205 | 1.00000 | .001000 | .000001 |
| Liter or Keg. | 61.0237 | .035315 | .001308 | 33.8140 | 2.11337 | 1.05669 | .264172 | 15432.3 | 32.1507 | 35.2739 | 2.67923 | 2.20462 | 1000.00 | 1.00000 | .001000 |
| Cu. M. | 61023.7 | 35.3146 | 1.30795 | 33814.0 | 2113.37 | 1056.69 | 264.172 | $154320_3$ | 32150.7 | 35273.9 | 2679.23 | 2204.62 | 1000000 | 1000.00 | 1.00000 |

Note. The small subnumeral following a zero indicates that the zero is to be taken that number of times: thus, $.0_31428$ is equivalent to .0001428.

Values used in constructing table:

1 inch = 2.540001 cm.

∴ 1 cu. in. = 16.387083 cc. = 16.387083 g $H_2O$ at 4°C = 39°F.

231 cu. in. = 1 gallon = 3785.4162 g.

1 lb. av. = 453.5926 g.

∴ 1 gal. = 8.34541 lb.

∴ 1 lb. av. = 27.679886 cu. in. $H_2O$ at 4°C.

1 lb. av. = 7000 grains

∴ 1 gallon = 58417.87 grains

# TABLES AND USEFUL DATA

## XV.—USEFUL MEMORANDA

### Gas Calculations

**Conversion Formulae for Gas Volumes.** Conversion from existing to standard conditions,

$$V = \frac{V' \times 273 \times (P - w)}{273 + t \times 760}.$$

Gas at standard volume to new conditions of temperature and pressure

$$V' = \frac{V \times 273 + t \times 760}{273 \times (P - w)}$$

$V$ = standard volume, $V'$ = volume under other conditions of temperature and pressure (other than 0° C. and 760 mm. Hg pressure).

$t$ = temperature of the gas, $P$ = barometric pressure in mm. Hg + static pressure of the gas. $w$ = water vapor pressure at temperature and pressure that the gas is measured or to which it is to be converted.

**Petot Formulae for Measuring the Velocity of a Gas in a Flue.**

*A.* Simple formula for fair approximations $V = 42\sqrt{h}$.

*B.* More exact formula $V = 1290 \dfrac{\sqrt{\frac{1}{2}h(1 + .00217t)}}{BM}$.

$V$ = velocity in feet per second. $h$ = gauge reading in terms of water, i.e., the total differential in terms of vertical reading. In a gauge inclined 1 : 10, with ether in place of water, 10″ differential = 10 × .72 ÷ 10 = .72. In the formula $B$ ½ the reading is taken as the deflection due to velocity pressure is half the total deflection (proven by repeated tests, suction is producted by the gas flow on the straight petot arm). Allowance is made for this in formula *A*. $t$ = temperature of the gas measured. $B$ = barometric pressure + plus static pressure of the gas in terms of inches of mercury (air standard 29.92″). $M$ = specific gravity of the gas compared with the hydrogen molecule $H_2$ = 2.016.

To obtain the specific gravity of a gas, multiply the molecular weight of each constituent by its per cent ratio in the mixture, divide by 100 and finally divide the sum of these results by 2.016.

*Examples.* The sp.gr. of a gas having the composition 87% nitrogen, 5% oxygen, and 8% sulphur dioxide we would find

28.02 ($N_2$) × 87 ÷ 100 = 24.38
32.00 ($O_2$) × 5 " = 1.6
64.06 ($SO_2$) × 8 " = 5.12 total = 31.1 sp.gr. $= \dfrac{31.1}{2.016} = 15.42.$

The sp.gr. of air containing 78% nitrogen, 21% oxygen, 1% argon would be

28.02 × .78 = 21.86,
32.00 × .21 = 6.72,
39.88 × .1 = 0.4 total = 28.98 sp.gr. = 14.38.

Consult table XXIII.

The gram molecular weight of any gas occupies 22.4 liters.

## XV. (Continued) — Other Data

1 cubic foot of water weighs 62.37 pounds.

1 gallon (U. S.) of water weighs 8.33 pounds (the British gallon is 20% more than the U. S.).

1 liter of water weighs approximately 2.2 pounds.

### Areas of Plane Figures

**Area of any triangle** = $\frac{1}{2}$ base multiplied by the altitude.

**Rectangle.** Area = base multiplied by altitude, i.e., multiply the length of one side by the length of a perpendicular side.

**Parallelogram.** Area = multiply the length of one side by the vertical distance to the parallel side.

**Trapezoid.** Area = multiply half the sum of the parallel sides by the perpendicular distance between the two.

**Circle.** Area = $0.7854d^2$, or $\pi r^2$ or $\frac{1}{2}Cr$, or $\frac{1}{4}Cd$.

$\pi = 3.1416$, $r$ = radius, $C$ = circumference, $d$ = diameter.

### Volumes of Solids

**Regular Prism.** Area = $\frac{1}{2}nrah$, or $Bh$.

$n$ = number of sides, $r$ = perpendicular from center of base to sides of the base, $h$ = height of prism, $B$ = area of base.

Lateral area = $2\pi rh$.

**Right Circular Cylinder.** Volume = $\pi r^2h$ also $Bh$. Lateral area = $2\pi rh$.

**Regular Pyramid.** Volume = $\frac{1}{3}$ altitude multiplied by area of base.

**Right Circular Cone.** Volume = $\frac{1}{3}\pi rh$. Lateral area = $\pi rs$.

$r$ = radius of base, $s$ = slant height or $\sqrt{r^2 + h^2}$.

**Sphere.** Volume = $4/3\pi r^3$, or $4.189r^3$. Area = $4r^2$ or $3.1416d^2$.

**Barrel or Cask.** Approximate gallons = $.0034n^2h$ where $n$ = mean diameter of barrel. $h$ = height, both measurements in inches.

## TABLES AND USEFUL DATA

### Definitions

#### Heat

*Calorie* is 1/100 of the heat required to raise the temperature of one gram of water from 0° C. to 100° C.

One kilogram calorie = 1000 gram calories or 3.968 B.t.u.

*Latent heat of evaporation* is the quantity of heat required to convert 1 gram of a liquid into vapor without change of temperature.

*Latent heat of fusion* is the quantity of heat required to change a gram of the substance from a solid to a liquid state without changing temperature.

*Specific heat.* The British thermal unit (B.t.u.) = 1/180 part of the heat required to raise the temperature of one pound of water from 32° F. to 212° F.

*Specific heat* of a body is the quantity of heat required to raise the temperature of a unit weight of that body one degree, C.

#### Photometry

*Lux.* This is the practical unit of illumination and is the light received from a source of 1 meter distance.

*Foot-candle.* This is the illumination received by a standard candle at one foot distance. The candle loses in burning 120 grams per hour.

1 foot-candle = 10.76 lux.

*Candle-power.* The comparison of the illumination of a light with one standard candle. A simple method for determination is to place the light and the burning candle 60 inches apart (2 meters and 100 inches distance also taken). A screen with a spot of oil is so placed between the lights as to receive a uniform illumination on each side, which is readily seen by the spot. The square of the distance from the screen to the light tested divided by the square of the distance from the screen to the standard candle = the candle-power of the light. When gas is tested the flame is so regulated that it burns 5 cubic feet of gas an hour. The standard candle burns 120 grams per hour as stated above.

#### Units in Electricity

*Ampere* is the unit of current flow. An ampere will deposit from a silver nitrate solution 1.118 milligrams of silver (.001118 g.) per second.

*Coulomb* is the unit of quantity. One coulomb will deposit .001118 g. Ag (time factor not considered as in case of ampere). 96,494 coulombs will deposit the gram equivalent of an element from a solution of its salt, i.e., 107.88 grams of silver, $\frac{63.57}{2}$ grams of cupric copper $Cu^{++}$ $\frac{55.84}{3}$ of ferric iron $Fe^{+++}$, 63.57 of cuprous copper $Cu^{+}$, $\frac{55.84}{2}$ gram of ferrous iron $Fe^{++}$, etc. One gram equivalent of an element carries 96,500 (round numbers) coulombs.

*Electromotive force*—E.M.F.—is the force causing electricity to move.

*Erg.* This is the unit of power and is the force which applied to the standard gram body would give that body an acceleration of 1 cm. per second.

## TABLES AND USEFUL DATA

*Dyne* = the force which acting on one gram for one second produces a velocity of one centimeter per second.

*Joule.* This is the practical unit of electrical energy and is produced when a steady current of one coulomb per second, i.e., one ampere, passes through a resistance of one ohm for one second.

*Ohm.* This is the resistance that is offered at 0° C. by a column of mercury 106.3 centimeters long, being 1 square millimeter in cross section and weighing 14.4521 grams.

*Volt.* This is the electromotive force which produces one ampere of current through a conductor having a resistance of one ohm.

If any two of the factors are known the third can be found by the formula $I = E/R$; $I$ = ampere current, $E$ = electromotive force (volts) and $R$ = ohms resistance.

*Watt.* One watt is produced when one ampere of current flows under a pressure of one volt (E.M.F.).

One watt = .00134 horse power, = 44.25 foot pounds, per minute, = 14.33 gram calories per minute, = .057 B.t.u. per minute.

*Watt-hour* and kilowatt-hour are the units of energy used in commercial electrical work.

Watt-hour = 3600 joules, = 2655.4 ft. lbs., = 859975 gram calories, = 3.412 B.t.u. = .001341 h.p. hr.

One kilowatt = 1000 watts.

### Other Terms

*Foot-pound* is the unit of work done in raising a weight of one pound through a distance of one foot. Work = weight multiplied by height, or force multiplied by distance.

*Horse power* = 550 foot pounds.

*Specific gravity* of a substance is the ratio of the weight of a given volume of that substance compared with the weight of an equal volume of water.

*a.* Solid heavier than water. Weight of solid in the air divided by the difference between this weight and its weight in water = sp.gr. of solid.

*b.* Solid lighter than water. The weight of the solid in the air divided by this weight + the loss of weight of a sinker due to the buoyancy of the solid = sp.gr.

*c.* Solid soluble in water. Determine gravity in a liquid in which it is insoluble whose specific gravity is known, multiply the gravity in terms of the liquid by the gravity of the liquid = sp.gr. in terms of water.

*d.* Liquids. Compare with water by weighing in a specific gravity bottle; the bottle being filled with water is weighed, the bottle, drained and dried, is filled with the liquid and again weighed; the weights are compared on subtracting the weight of the empty bottle.

*e.* The loss of weight of an insoluble substance immersed in the liquid is divided by the loss of weight of the substance immersed in water = sp.gr.

*f.* The specific gravity is determined by the hydrometer.

## ABBREVIATIONS

[a] specific rotation
([a])$^{20}_{D}$. . for 20° and sodium light)
abs. absolute
Ac acetyl (AcH, acetaldehyde; AcOH, acetic acid)
a. c. alternating current
alc. alcohol
alk. alkaline
Am amyl
amp. ampere(s)
amt. amount
app. apparatus
approx. approximate, approximately
aq. aqueous
at. atomic
atm. atmosphere(s), atmospheric
at. wt. atomic weight
av. average
b. (followed by a figure denoting temperature) boils at, boiling at (similarly $b_{13}$, at 13 mm. pressure)
bacteriol. bacteriological
b. p. boiling point
B. t. u. British thermal unit(s)
Bu butyl (normal)
Bz benzoyl (BzH, benzaldehyde; BzOH, benzoic acid)
cal. calorie(s)
calc. calculate
calcd. calculated
calcg. calculating
calcn. calculation
cc. cubic centimeter(s)
chem. chemical
cm. centimeter(s)
coeff. coefficient
com. commercial
compd. compound
compn. composition
concd. concentrated
concn. concentration
cond. conductivity
const. constant
contg. containing
cor. corrected
c. p. candle power
c. p. chemically pure
cryst. crystalline
crystd. crystallized
crystn. crystallization
cu. m. cubic meter(s)
d. density ($d_{13}$, specific gravity at 13° referred to water at 4°; $d^{20}_{20}$, at 20° referred to water at the same temperature)
d. c. direct current
decompn. decomposition
deriv. derivative
det. determine
detd. determined
detg. determining
detn. determination
dil. dilute
diln. dilution
distd. distilled
distg. distilling
distn. distillation
elec. electric, electrical
e. m. f. electromotive force
equil. equilibrium
equiv. equivalent
est. estimate
estd. estimated
estg. estimating
estn. estimation
Et ethyl ($Et_2O$, ethyl ether)
evap. evaporate
evapd. evaporated
evapg. evaporating
evapn. evaporation
examd. examined
examg. examining
examn. examination
expt. experiment
exptl. experimental
ext. extract
extd. extracted
extg. extracting
extn. extraction
f. p. freezing point
ft. foot, feet
g. gram(s)
h. p. horse power
hr. hour
in. inch
inorg. inorganic
insol. insoluble
kg. kilogram(s)
kw. kilowatt(s)
l. liter(s)
lab. laboratory
manuf. manufacture

max. maximum
mfg. manufacturing
m. meter(s); (also followed by a figure denoting temperature) melts at, melting at
Me. methyl
min. minute(s)
mixt. mixture
mol. molecular, molecule
mol. wt. molecular weight
m. p. melting point
$n$ index of refraction ($n_D^{20}$, for 20° and sodium light)
$N$ normal
org. organic
pathol. pathological
p. d. potential difference
Ph phenyl
pharmacol. pharmacological
physiol. physiological
p. p. m. parts per million
ppt. precipitate
pptd. precipitated
pptg. precipitating
pptn. precipitation
Pr. propyl
prep. prepare
prepd. prepared
prepg. preparing
prepn. preparation
qual. qualitative
quant. quantitative
recrystd. recrystallized
resp. respectively
r. p. m. revolutions per minute
sapon. saponification
sapond. saponified
sapong. saponifying
sat. saturate
satd. saturated
satg. saturating
satn. saturation
sec. second(s)
sep. separate
sepd. separated
sepg. separating
sepn. separation
sol. soluble
soln. solution
soly. solubility
sp. specific
sp.gr. specific gravity
sq. cm. square centimeter(s)
sym. symmetrical
temp. temperature
U. S. P. United States Pharmacopeia
v. volt(s)
vol. volume
w. watt(s)
w. p. c. watts per candle
wt. weight

## GENERAL REFERENCES

### General References


Allen, A. H., Organic Analysis, v. 1–8, 4th Ed., 1909–1913. P. Blakiston's Son & Co.

Arnold and Mandel, Compendium of Chemistry. John Wiley & Sons, New York. 1904.

Authenrieth, W., and Warren, W. H., Laboratory Manual for the Detection of Poisons. 1921. P. Blakiston's Son & Co., Philadelphia, Pa.

Baskerville, C., and Curtman, L. J., Quantitative Analysis, 1910. The Macmillan Co.

Blair, A. A., The Chemical Analysis of Iron, 7th Ed., 1918. Lippincott & Co., Philadelphia, Pa.

Brearly, H., and Ibbotson, F., The Analysis of Steel Works Materials, 1902. Longmans, Green & Co., London and New York.

Browning, P. E., Introduction to the Rarer Elements, 3d Ed., 1919. John Wiley & Sons, New York.

Cahen, E. and Wootton, W. O., The Mineralogy of Rarer Metals, 1920. J. B. Lippincott Co.

Carins, F. A., Quantitative Chemical Analysis, 3d Ed., 1896. H. Holt & Co., New York.

Clowes and Coleman, Quantitative Analysis, 5th Ed. P. Blakiston's Son & Co.

Classen, A., Quantitative Analysis. Translated by N. H. Harriman, 1902. Geo. Wahr, Pub., Ann Arbor, Mich.

Comey, A. M., Dictionary of Chemical Solubilities. 1921. Macmillan & Co.

Crookes, W., Select Methods in Chemical Analysis, 4th Ed., 1905. Longmans, Green & Co., New York, London. 1905.

Dennis, L. M., Gas Analysis. Macmillan & Co., New York. 1913.

Fresenius, K. M., Quantitative Chemical Analysis, 6th Ed. Translated by A. I. Cohn, 1911. John Wiley & Sons, New York. 1912.

Ibid., Qualitative Chemical Analysis. Trans. 17 Ed., 1921, by C. A. Mitchell. J Wiley and Sons.

Fulton, C. M., Fire Assaying, 2d Ed., 1911. McGraw-Hill Co., New York. 1911.

Furman, H. Van F., Practical Assaying, 5th Ed., 1901. John Wiley & Sons, New York.

Gardner, H. A., Paint Technology and Tests, 1911. McGraw-Hill Book Co., New York.

Gardner, H. A., and Schaeffer, J. A., Analysis of Paints and Painting Materials, 1911. McGraw-Hill Book Co., New York.

Griffin, Technical Methods of Analysis, 1921. McGraw-Hill.

Gill, A. H., Gas and Fuel Analysis for Engineers, 3d Ed., 1903. J. Wiley & Sons, New York.

Gill, A. H., A Short Hand-book of Oil Analysis, 6th Ed., 1911. J. B. Lippincott Co., 1919, Philadelphia and London.

Gooch, F. A., Methods in Chemical Analysis, 1912. John Wiley & Sons, New York.

Hempel, W., Gas Analysis. Macmillan & Co., New York.

Hillebrand, W. F., The Analysis of Silicate and Carbonate Rocks, Bull. 422, U. S. Geological Survey, 1910. Washington Gov. Print. Office.

Johnson, C. M., Rapid Methods for the Chemical Analysis of Special Steels, 2d Ed., 1920, 1914. John Wiley & Sons, New York.

Julian, F. A., Text Book of Quantitative Analysis, 1902. Ramsey Publishing Co., St. Paul, Minn.

Langbein, Electro Deposition of Metals. 1920. H. C. Baird & Co.

Leach, A. E., Food Inspection and Analysis, 4th Ed., 1920, John Wiley & Sons, New York.

Levy, S. I., The Rare Earths, 1915. Edward Arnold Pub.

## GENERAL REFERENCES


Lewkowitsch, J., Chemical Analysis of Oils, Fats, Waxes, 1913–1916. The Macmillan Co.

Liddell, Metallurgists and Chemists' Handbook. 1918.

Low, A. H., Technical Methods of Ore Analysis, 9th Ed., 1922. John Wiley & Sons, New York.

Lunge, G., The Manufacture of Sulphuric Acid and Alkali, 4th Ed., 1913. Van Nostrand Co., New York.

Lunge, G., Technical Methods of Chemical Analysis. Trans. Edited by Chas. A. Keane. Gurney & Jackson, London. D. Van Nostrand Co., New York.

Mahin, E. G., Quantitative Analysis, 1919. McGraw-Hill Book Co.

Marks, L. S., Mechanical Engineers' Handbook, 1916, McGraw-Hill Book Co.

Mead, R. K., Portland Cement, 2d Ed., 1911. The Chemical Pub. Co., Easton, Pa. Ibid., Chemists' Pocket Manual, The Chemical Pub. Co., Easton, Pa.

Mellor, J. W., Treatise on Quantitative Inorganic Analysis, 1913. Chas. Griffin & Co., Ltd., London.

Olsen, J. C., Quantitative Chemical Analysis, 5th Ed., 1921. D. Van Nostrand Company, New York.

Perkin, F. M., Electro Chemistry. Longmans, Green & Co., London and New York. 1905.

Prescott, A. B., and Johnson, O. C., Qualitative Chemical Analysis, 7th Ed., 1920. Revised by J. C. Olsen. D. Van Nostrand Co., New York.

Rhead, E. L., and Sexton, A. H., Assaying and Metallurgical Analysis, 2d Ed., 1911. Longmans, Green & Co., London and New York.

Rogers, A., Manual of Industrial Chemistry, 3d Ed., 1921. D. Van Nostrand Co.

Roscoe, H. E., and Schorlemmer, C., Treatise on Chemistry, 1911. Macmillan & Co.

Scott, W. W., Qualitative Analysis, 4th Ed., 1921. D. Van Nostrand Co., New York.

Segerblom, W., Tables of Properties. Exeter Book Pub. Co., Exeter, N. H.

Seidell, A., Solubilities of Inorganic and Organic Substances, Second Ed., 1919. D. Van Nostrand Co., New York.

Smith, E. F., Electro-analysis. P. Blakiston's Son & Co. 1918.

Stillman, T. B., Engineering Chemistry, 5th Ed., 1916. The Chemical Publishing Co., Easton, Pa.

Sutton, F. A., Systematic Handbook of Volumetric Analysis, 10th Ed., 1911. P. Blakiston's Son & Co., Philadelphia.

Talbot, H. P., An Introductory Course in Quantitative Chemical Analysis, 1899. Macmillan & Co., New York.

Thorpe, E., A Dictionary of Applied Chemistry, Five Volumes, 1913. Longmans, Green & Co., London and New York.

Treadwell, E. P., Analytical Chemistry. Translated by W. T. Hall, 4th Ed., 1914. J. Wiley & Sons, New York.

Van Nostrand's Chemical Annual. Edited by J. C. Olsen, 5th Issue, 1922. D. Van Nostrand Company, New York.

White, C. H., Methods in Metallurgical Analysis, 1915. D. Van Nostrand Co., New York.

Wiley, H. W., Principles and Practice of Agricultural Analysis, 1914. The Chemical Pub. Co., Easton, Pa.

# INDEX

# PLAN OF INDEX

The subjects are listed according to the following outline.
General subjects (in alphabetical order)
Element, chapter on, pages . . . to . . .
" detection by (methods in alphabetical order)
" determ. by gravimetric methods
methods given in alphabetical order
" determ. by volumetric methods
methods given in alphabetical order
" determ. in (alphabetical order of subjects)
" minerals and occurrence
prep. and sol. of sample
properties
separations, special procedures, etc.
Compounds of element (alphabetical order)

# INDEX


Abbreviations, list of, 849
Acetic acid, strength determining, 776
**Acidimetry** and alkalimetry, chapter, 661–681
Acidimetry and Alkalimetry alkalies, analysis of:
ammonia, 680
potassium hydroxide, 679
sodium hydroxide, 677
hydrometer m., 675
indicators, 661, 662, 663
inorganic acids, analysis of:
muriatic (hydrochloric), 674
sulphuric, 676
Acidimetric-alkalimetric methods, introduction, 5
Acidimetric and Alkalimetric standard:
Acid, benzoic, 667
hydrochloric, 666
sulphuric, 665, 666
Alkali hydroxide, 667
standard burettes, 668
standards, ultimate, 664
weighing acids:
apparatus for, 671, 672, 673
nonvolatile acids, 670
volatile acids, 670
**Acid** method for molybdenum, 389
Acid, standard, preparation of, 665
inorganic, analysis of, 674–676
free in presence of iron, 681
weighing of, 670–673
Acidity and alkalinity of water, 741, 742
**Acker** process for tin, determining, 584
**Air,** analysis of, 769
composition of, 410
**Alcohol,** Ethyl, preparation of pure, 776
methyl, 149
**Alizarin** S. test for aluminum, 76
colorimetric method, 84
**Alkalies,** preparation and solution, 462
in silicates, J. L. S. method, 473
hydroxides:
ammonium hydroxide, analysis of, 680
potassium hydroxide, analysis of, 679
sodium hydroxide, analysis of, 677
hydroxides and carbonates, detection of, 461
procedure for fertilizers, 462
procedure for soils, 462
separations, 463–466
from Al, Ba, Ca, Cr, Fe, Si, etc.
from Mg, barium hydroxide method, 465
ditto by ammonium phosphate method, 465
potassium from sodium, 466
separation from each other, 466
solution of rocks, etc., 462
Alkalies, 460–481
combinations, 480
hydrofluoric acid method for, 475
in detection of palladium, 429
Alkalimetric method for phosphorus, 442
for phosphorus in iron and steel, 332
Alkaline earths, direct precipitation of, 119
preliminary considerations of, 118
separations from elements, 119
separation of, 120
**Alloys,** chapter on, 682–689
brass or bronze, analysis of, 686
determination of arsenic and antimony, 686
cadmium and copper, 687
copper and lead by elect., 688
lead as sulphate, 687
tin, 686
solution of the alloy, 686
of copper, phosphorus in, 443
detection of tungsten in, 603
determination antimony in, 93, 95
determination bismuth in, 140
determination cobalt in, 232
determination lead in, 339
determination nickel in, 401, 408
determination tin in, 576, 581
determination tungsten in, 606–609
determination vanadium in, 634
separation table of, 682
solubility of, 50
test for gold in, 279
type metal, analysis of, 683
determination of antimony in, 684
arsenic in, 685
copper and iron in, 683
lead in, 683
tin in, 684
solution of the alloy, 683

**Alpha** benzildioxime, preparation of, 778
detection of nickel, 399
Alpha ray method for determining radium, 483
**Alumina** in slags, 693
**Aluminum,** chapter on, 75 to 88
available in bauxite and clays, 84, 85
bauxite analysis of, 84
detection of, 76
alizarin S. test for, 76
cobalt nitrate test for, 76
sodium thiosulphate test for, 76
determination by gravimetric methods:
ammonium hydroxide method, 78
phosphate method, 83
determination by volumetric methods, 85
colorimetric method, 84
fluoride method, 85
determination in iron and steel, 83, 88
determination in lead, 354
in lead, 354
determination in water, 739
metallic, analysis of, 87
minerals and occurrence of, 75
preparation and solution of sample, 77, 78
phosphate, properties of, 83
purification of, 83
separation from chromium, 222
separation from other substances, 80, 81, 82
soluble in ores, 85
**Amblygonite,** 476
**Amino nitrosophenyl-hydroxylamine,** 308
**Ammonia,** detection of, 411
detection of palladium, 429
determination of by gravimetric method, 413
in water, 743
method for aluminum determination, 78
method for copper, traces of, 256
platinochloride method for ammonia, 413
Ammonium acetate extraction of lead, 340
chloride test for platinum, 449
chloride test for vanadium, 624
hydroxide, analysis of, 680
magnesium phosphate:
proportion of Mg as, 363
properties of, 365
volumetric method for, 366
persulphate method for manganese, 330, 378
phosphomolybdate method for phosphorus, 439
sulphide method for mercury, 383
sulphocyanate, *see* sulphocyanate
**Ampere,** 847
Analysis, limit of accuracy of, 16
preliminary considerations, 65
Analytical Methods, Part II, 75
Anemometer, 758
**Anglesite,** 336
**Anhydrite,** 168
**Antimonic,** distinction from antimonous salts, 90
**Antimony,** chapter on, 89 to 96
apparatus for determining small amounts, 96
detection of, 89
by hydrolysis, 90
by hydrogen sulphide, 90
traces of, 90
determination by gravimetric methods, 91
determination by volumetric methods, 91
bromate method, 93
iodine method, 94
permanganate method, 91
determination of traces of, 96
determination in alloys, *see* alloys
occurrence and minerals of, 89
properties of, 89
standard sol. prep. of, 778
**Apatite,** 433
Apothecaries' weight table, 842
Apparatus, cuts of, *see* under Contents
Apparatus for fire assay, 699 to 703
*see* list of illustrations following table of Contents
standard laboratory, 800 to 815
buoyancy constants, table of, 808
standardization of:
burettes, 807
flasks, 804
pipettes, 805
weights, 811
**Aragonite,** 167
Areas of plane figures, formulae, 846
**Argentite,** Silver glance, 48, 517
**Argol** for fire assay, 698
**Arrhenius,** electrolytic dissociation theory, 17
**Arsenates** and arsenites distinction, 98
**Arsenic,** chapter on, 97 to 114
detection of, 97
determination by gravimetric methods:
magnesium pyroarsenate method, 104
determination by volumetric methods:
potassium iodate method, 106
titration with iodine, 105
determination in ores, 107

Arsenic — determining small amounts of by Gutzeit method, 108
minerals and occurrence, 97
preservation of standard stains, 109
properties, 97
standard solution of, 108, 777
traces in acids, 111
**Arsenite** method for iodine, 293, 294
sol. tenth normal prep. of, 778
**Arsenolite,** 45
**Arsenopyrite,** 49
Ash determination in coal, 722
fusibility of in coal, 732
Assay, *see* fire assay
Assaying, *see* fire assay
slags, 707
ton system, 701
Atack's method for traces of aluminum, 84
Atmospheric air, analysis of, 769
Atomic weights, International table of, 816
Avogadro's hypothesis, 17
**Azurite,** blue copper carbonate, 240

Balance, description and rules for, 37 to 41
Balances and weights for assaying, 702, 704
**Barite,** 49, 115
**Barites,** analysis of, 129
**Barium,** chapter on, 115 to 130
detection of, 115
determination by gravimetric methods:
as chromate, 123
as sulphate, 123
determination by volumetric methods, 127 to 128
in insoluble residue, 117
minerals and occurrence, 115
separation from calcium, 121, 122
separation from strontium, 121, 122
separation from other elements, 121
acetate or chloride, test for chromium, 218
carbonate test for uranium, 615
chloride test for selenium, 500
hydroxide method for determining carbon, 197
sulphate in S determination, 539
sulphate method for sulphur, 542, 544
Barker's hydrometer method for carbon dioxide, 196
**Baryta,** detection of magnesium, 360
Basic acetate ppt. of iron and alumina, 370
**Bauxite,** 47, 75
analysis of, 84
available alumina in, 85
Bead-charcoal test for titanium, 587
Beaker and cover, 42
Beaumé and sp. gr. comparison, 840
Beginner's, courses for, 69
Beneker's modification of Eggertz' method for determining carbon, 192
**Benzidine** acetate test for gold, 280
hydrochloride, preparation of, 778
**Bichloride** of tin, methods for, 583 to 585
**Bismite,** bismuth ochre, 46, 131
**Bismuth,** chapter on, 131 to 142
detection of, 131
by reducing agents, 132
determination of by gravimetric methods:
as basic chloride, 136
cinchonine potassium iodide, 141
oxide, 135
in alloys, bearing metal, etc., 133, 140
in lead bullion, 133, 138, 350
in ores, 133
in ores and mattes, 140
minerals and occurrence of, 131
native, 131
separation from As, Sb, Sn, Mo, Te, Se, 134
from lead, 134
from mercury, 134
other elements, 134 to 135
standard solution, preparation of, 779
oxychloride, BiOCl, 136
Bismuthate method for manganese, 374
for manganese in steel, 331
**Bismuthinite,** 48, 131
**Bismutite,** 131
Bisulphate fusion method for determining radium, 488
Blast furnace gases, 767
slags, composition of, 690
Blast lamp, 61
Bleaching powder, evaluation of, 217
Blowpipe test for zinc, 637
**Blue vitriol,** copper in, 258
Boat and holder, carbon determination, 189
Boats, determining carbon in steel, 328
Bonardi, J. P., on thorium, 568
Bond, F. C., on silver, 527
Bone ash, composition of, 434
**Borax,** 143, 470
amount for fire assay, 707
evaluation of, 148
Boric acid, titration of, 148
**Bornite,** purple copper, 239

**Boron,** chapter on, 143 to 152
detection of by:
flame test, 143
turmeric test, 144
other tests, 143
determination by gravimetric method, 145
determination by volumetric methods, 148
determination in ores, silicates, enamels, 145
occurrence and minerals of, 143
Boronatrocalcite, ulexite, 143
Boyle's law, 17
**Brass** or **bronze,** analysis of, 686 to 689
Brass, copper and , lead in, 258
**Braunite,** 367
Breyer, F. G., on zinc, 643
**Brimstone,** analysis of, 553
**Brines,** alkali in, 463
Brinton and James method for cerium, 204
Briquettes, iron ore, sulphur in, 549
Bromate method for antimony, 93
Bromates, test for, 153
Bromide, precipitation as silver salt, 155
**Bromine,** chapter on, 153 to 157
detection of, 153
by carbon disulphide, 153
carbon tetrachloride, 153
magenta test, 153
silver nitrate test, 153
determination by gravimetric method, 155
a silver bromide, 155
determination by volumetric methods:
chlorine method, 156
Volhard's method, 156
determination of free, 156
occurrence of, 153
separation from other elements, 155
from heavy metals, 155
separation from silver and cyanides, 155
**Brucite,** 359
B.t.u. in coal, determination and calculation of, 726
**Bullion,** copper, fire assay of, 715
gold and silver, fire assay of, 716
lead, fire assay of, 714
Buoyancy, effect of, 814
Burette, reading of, 65
Burettes, standard, 668
standardization of, 807
Burkhard, W. E., weighing tube, 673
Burners, types of:
blast lamp, 61
Bunsen, 61
Meker, 61
Buvold's method for nitrites, 419
**Cadmium,** chapter on, 158 to 166
detection of, 158
by blowpipe test, 159
hydrogen sulphide test, 158
determination by gravimetric method as:
metal by electrolysis, 162
sulphate, 162
sulphide, 161
determination in alloys, 160
carbonates, 160
determination in lead, 353
ores, 160
determination in spelter, 162
occurrence and minerals of, 158
separation from:
antimony, arsenic, tin, 166
bismuth, copper, mercury, 166
lead, silica, 165
zinc, 166
**Caesium** and rubidium, detection of, 481
occurrence of, 481
**Calcite,** 167
**Calcium,** chapter on, 167 to 177
detection of by, 168
flame test, 168
other tests, 168
determination by gravimetric metn ods, 170
oxalate method, 170
determination by volumetric methods, 173
permanganate titration, 173
determination in cement analysis, 174
determination in water, 739
minerals and occurrence of, 167
other methods for, 177
rapid preliminary examination for, 169
separation from other elements, 170, 171, 172
spectrum of, 168
oxide in sand, 516
**Calomel,** horn mercury, 381
Calorie, 846
Calorific value of coal, 726
Calorimeter, use and standardization of for coal analysis, 731
**Carbon,** chapter on, 178 to 200
detection of element, 179
determination of, 182, 186
Beneker's method, 192
determination by volumetric methods, 197
combined, colorimetric method, 190
combined, indirect method for determination of, 189
graphitic determination of, 189
in alloys, 180

Carbon — in coal, fixed, 726
in coal, volatile, 723
in iron and steel, 180, 327
colorimetric method for, 327
total by combustion, 327
carbon in graphite, 192
minerals and occurrence of, 178
preparation of sample for, 180
separation of from iron, 180
separation from other substances, 180
tubes, combined carbon determination, 191
**Carbonates,** bicarbonates, hydroxide tests for, 462
carbon dioxide determination, 193
$CO_2$ in, by hydrometer, 195
types and solubility, 45
**Carbon-dioxide,** barium hydroxide method for, 197
carbonates, detection of, 179
determination in air, 770
determination in carbonates, 193
in carbonates, hydrometer method, 196
loss of weight, method for, 195
**Carbonic acid,** free, detection of, 179
free in water, 742
**Carbon-monoxide,** detection of, 179
determination in air, 772
**Carbon-tetrachloride** test for bromine, 153
**Carnallite,** 460, 481
**Carnotite,** 614
Cassel's method for gold, 285
Casserole, introduction, 42
**Cassiterite,** 46, 571
**Celestite,** 49, 531
Cement, Portland, analysis of, 174
**Cerargyrite,** 518
**Cerium,** chapter on, 201 to 206
detection of, 201
estimation of, 202
by iodate method, 204
in Welsbach mantles, 205
minerals and occurrence of, 201
separation from other rare earths, 202
separation from thorium, 203
table of separations of rare earths, 206
**Cerussite,** 336
**Chalcocite,** 48
copper glance, 239
**Chalcopyrite,** copper pyrites, 239
Chapin, method of, for boron, 148
Charle's law, 18
Chiddey method for cyanide solutions, 718
Chili saltpeter, 470
Chimney and flue gases, 764
**Chloride** in presence of bromide and iodide, detection of, 207
Chlorides, silver nitrate test for, 207
test for silver, 518
water insoluble, 210
water soluble, 209
**Chlorine,** chapter on, 207 to 217
bromine and iodine in a mixture, 217
detection of, 207
free detection of, 207
determination by gravimetric methods, 208
as silver chloride, 211
determination by volumetric methods, 214
Mohr's method, 215
Volhard's method, 214
free, method for, 216
in bleaching powder, 217
in cement, copper, and copper ores, 217
in electrolytic gases, 767
in rocks and cinders, 210
in water, 743
method for determining bromine, 156
occurrence of, 207
separations from the halides, heavy metals, 210
**Chloroplatinate,** method for potassium, 467
Lindo-Gladding method, 468
**Chromate** (potassium) detection of lead, 337
method for lead, gravimetric, 342
volumetric, 345
gravimetric method for barium, 125
volumetric method for lead, 345
Chrome-iron ores, decomposition of, 220
**Chromite,** 46, 218
chromium in, 228
**Chromium,** chapter on, 218 to 229
comparison with vanadium, 624
detection of, 218
determination by gravimetric method, 223
hydroxide precipitation, 223
determination by volumetric methods, 224
ferrous sulphate method, 226
potassium iodide method, 224
in chromite, 228
in iron and steel, 221
in silicious materials, 219
in solubie chromate, 228
in steel, rapid method, 228
minerals and occurrence of, 218
separation from alumina, 222
separation from iron and alumina, 221

Chromium — small amounts by diphenyl carbazide method, 228
**Cinchonine** potassium iodide method for bismuth, 141
potassium iodide reagent, 141
Cinchonine potassium iodide sol., 779
reagent for tungsten, 609, 610
Cinders, sulphur in, 547
**Cinnabar,** 48, 381
Clays, available alumina in, 85
**Coal,** chapter on, 718 to 735
analysis of, determining ash, 722
calculation of B.t.u., 729
calorific value, 726
fixed carbon, 726
fusibility of coal ash, 732
Jackson's turbidimeter table, 724, 725
moisture, 722
volatile combustible matter, 723
volatile sulphur, 723
wet to dry basis, calculation of, 734
apparatus for preparing, 720
composition, 765
buckwheat, B.t.u. value, 730
preparation of sample, 719
sampling of, 719
**Cobalt,** chapter on, 230
detection of, 231
gravimetric methods for, 232
and nickel, determination in lead, 355
in metal cobalt, nickel and alloys, 232
in ores, 232
minerals and occurrence of, 230
separation (with Ni) from manganese, 233
separation from other elements, 232
**Cobaltite,** 230
Cobalt-nitrate test for aluminum, 76
Cochineal, preparation of solution, 798
Coin ingots, analysis of, 529
**Colemanite,** 143
Collection of gross sample, 21
Colloidal condition, 4
Colloids, precipitation of, 4
Color comparator, carbon determination, 191
Colorimetric method for gold, 285
for manganese, 378
Colorimetric-peroxide method for titanium, 597
Colorimetric processes, 7
**Columbite,** 559
Columbium, *see also* tantalum
Combinations, hypothetical in water, 752
Combustion method for carbon, 327
Commercial valuation of Al ores, 84
Common ion effect, law of, 17
Common salt for fire assay, 699
Complex ions, law of, 17
Cone and quartering sampling, 28
Conservation of mass, law of, 17
Conservation, thermo, law of, 18
Constant proportion, law of, 17
Containers, 34
Conversion factors, 824
**Copper,** 49
Copper, chapter on, 239 to 259
Copper, detection of, 240
determination by gravimetric methods:
electrolytic methods:
Rapid method of Heath, 245
from ammoniacal sol., 246
nitric acid sol., 246
by rotating anode, 247
Slow methods — blister copper:
large portion method, 250
small portion method, 248
notes, 251
hydrogen sulphide reduction method, 257
determ. by volumetric methods, 253
ammonia method, 256
ferrocyanide method, 253
potassium iodide method, 253
for ores, 254
(and lead) determination in brass, 258
determination in blue vitriol, 258
determination in lead, 353
in refined copper, 257
determination in slags, 695
determination in steel, 258, 259
hydrogen reduction of, 257
isolation of by:
electrolysis, 245
thiocyanate method, 243
positive element, 244
methods, preparation and solution of sample, 242
metals, 242
ores, 242
sulphides, matte, oxidized ores, 242
minerals and occurrence of, 239
separations, *see* isolation
solution of, 255
standard solution, preparation of, 780
alloys, phosphorus in, 443
bullion, fire assay of, 715
deposits, character of, 251
Corrosive action of water, 750
**Corundum,** 46, 75
Coulomb, 847

Coulomb's law, 19
Courses, outline of, 60, 70, 71
**Crocoite,** 218
Crucible, 703
assay, 703
charges in fire assay, 709
platinum, 62
porcelain, 62
Crushers, 28, 29, 30, 31
**Cryolite,** 75, 470
Crystallization, water of, determination, 65, 66
Cupellation in fire assay, 710
Cupels, 700, 703
Cupel-tongs, 702
**Cupferron,** precipitation of iron, 308
**Cupric potassium,** chloride method for separation of carbon from iron and steel, 180
**Cuprite,** 46
ruby copper ore, 240
Cuprous chloride, acid and ammoniacal for gas analysis, 781
detection of palladium, 429
Cyanide method for determining silver, 522
of potassium method for nickel, 496
solutions, assay of, 718
**Cyanogen,** detection of, 198

Dalton's atomic theory, 17
Dalton-Henry's law, 17
**Danburite,** 143
**Datolite,** 143
Davison's scrubber apparatus, 416
Decomposition of material, 44
substances, rules for, 50
Definitions, heat, photometry, electrical units, etc., 847 to 848
Dely weighing tube, 671
Demonstration method, 71
Deposits, character of copper, 251
Derby on gold, 278
Deshey's method for manganese in steel, 330
Desiccator, 64
Devarda's alloy, preparation of, 780
Diamonds, varieties of, 178
Dichromate method for barium, 127
reagent, standard, *see* potassium dichromate, 786, 787
Dicyandiamidine sulphate test for cobalt, 231
**Dimethylglyoxime,** detection of nickel, 398
method for nickel, 402
reagent for nickel, 403
**Diphenyl** carbazide reagent, preparation of, 780
**Diphenylamine** test for nitrates, 412
Diphenyl carbazide method for chromium, 228
preparation of, 229
Dissociation, electrolytic theory of, 17
**Dolomite,** 45, 167, 359
Doré bullion, fire assay of, 716
Dry to wet and wet to dry, calculation of, 734
Duboscq colorimeter, 358
Dulong-Petit's law, 17
Dyne, 848

Electric-furnace, 62
Electrolytic gases, analysis of, 767
method for cadmium, 162
copper, 245 to 252
gold, 282
lead, 344
mercury, 384
silver, 522
zinc, 642
methods, 7
Electromotive force, 847
series, 17, 818
Emanation method for radium, 484
Enamels, boron in, 145
cobalt in, 238
End-point, definition of, 5
Energy conversion factors, 843
Erg, 847
Erlenmeyer flask, 42
Eschka's method for sulphur in coal, 539
Etching test for fluorine, 261
Ether method for removal of iron from a solution, 306
test for chromium, 218
Evolution method for sulphur in iron and steel, etc., 333, 547
Exit gases, $SO_2$ in, 555

Faraday's law, 18
Fehling's solution, preparation of, 780
**Ferberite,** 602
**Ferric hydroxide** occlusion of lead, 356
iron, determination, *see* Iron
Ferric salts in determination iodide, 294
titration of titanium, 595
Ferro-carbon titanium analysis, 593
**Ferrocyanide** method for copper, 256
method for zinc, 244
by external indicator, rapid method, 648
by internal indicator, 643
insoluble zinc material, notes on, 645
Ferrocyanide standard reagent, *see* potassium ferrocyanide, 788
test for copper, 241
uranium, 615

Ferrocyanide — test for zinc, 637
Ferro and ferri cyanides, determination of, 200
**Ferro-tungsten,** tungsten in, 609
**Ferrous** iron, determination, *see* Iron
sulphate method for chromium, 226
sulphate reagent, 782
Fertilizers, alkalies in, 462
Filters, types of, 57
Filtering precipitates for ignition, 58
Filtration, general directions for, 57
Fire assay for gold and silver, chapter on, 697 to 718
assay slags, 707
borax amount for, 707
crucible assay, 703
crucible charges, 709
cupellation, 710
cyanide solutions, 718
of bullion, 714, 715, 716
copper bullion, 715
gold and silver bullion, 716
lead bullion, 714
furnaces and equipment for, 699 to 703
fusing the charge, 708
lead reduction with oxidized ores, 703
lead reduction with sulphide ores, 704
litharge, amount for, 705
parting, 712
reagents for, 698, 699
scorification assay, 709
sodium carbonate amount in, 706
weighing and mixi ng, 707
Fitzpatrick apparatus for determining antimony, 96
Fixed carbon in coal, 7 26
Flame test for copper, 240
strontium, 531
Flasks, standardization of, 804
Fleming's apparatus for determining carbon in iron and steel, 183
Flow meter, 758
Fluid measure table, 842
**Fluorine,** chapter on, 260 to 274
detection of, 260
etching test of, 261
hanging drop test, 260
other tests, 262
determination gravimetric as:
calcium fluoride, 264
lead chlorofluoride, 265
determination volumetric by:
colorimetric method, 267
Offerman's method modified, 266
fluorspar, evaluation of, 272
sodium fluoride, analysis of, 273
minerals and occurrence of, 260
preparation of sample, 263
calcium fluoride, 263
fluorspar, 263
silicic acid removal, 263
silicious ores and slags, 263
traces of, 271
**Fluorite,** 167
**Fluorspar,** valuation of, 263, 272
Foaming and priming of water, 750
**Franklinite,** 636
Free, *see* noun i.e., free chlorine
*see* chlorine, free
Fresenius method for iodine, 295
Foot-candle, 847
Foot-pound, 848
Funnels for filtration, types of, 57, 58
Furnace and combustion tube for determining carbon, 183
Fusion method for molybdenum, 389
nickel ores, 400, 401
in S determination, 538
methods of making, 43
methods with potassium bisulphate, 305
sodium carbonate, 305
Furnaces for fire assay, 699

**Galena** (galenite), 48, 398
Gamma ray method for determining radium, 489
**Garnierite,** noumeit, 398
**Gas** analysis, chapter on, 754 to 774
atmospheric air, 769
bacteria in determination, 773
carbon dioxide determination, 770
carbon monoxide determination, 772
moisture, 768
ozone, 771
sulphur dioxide, 554
chimney and flue, 764
carbonic acid indicators, 764
coal, composition of, 765
smoke, 766
temperature, 764
electrolytic gases, 767
chlorine determination, 767
analysis of, general:
apparatus, Orsat, description, 759
carbon dioxide determination, 761
carbon monoxide determination, 762
hydrocarbons determination, 762
oxygen determination, 761
mine gases, 768
carbon monoxide determination, 768
methane determination, 768
producer and fuel, blast furnace gases, 767

Gas calculations, 845
calorific power table of various gases, 773
mantles, solution of, 565
measurement of large quantities, 757
anemometer, 758
flow meter, 758
orifice meter, 758
pitot tube, 757
wet meter, 757
measurement of small quantities, 759
Hempel apparatus, 759
Orsat apparatus, 759
Scott's apparatus, 558
moisture in, 68
oxygen determination, 427
sampling of, 754
Gay-Lussac's law, 18
method for silver, 524
apparatus for determining silver, 525
Geissler bulb, 181
Gerhardt bulb, 181
Gibbs, W., on magnesium, 363
Gill, A. H., on gas analysis, 754, 774
Glacial acetic acid method for uranium, 620
Glauber salt, 470
**Glucinum,** chapter on, 275 to 277
detection of, 275
method for determining, 277
occurrence of, 275
solution of sample, 276
separation from other elements, 276, 277
**Glycerol** in boron determination, 148
Gold, 49
bullion, fire assay of, 717
chapter on, 278 to 286
detection of, 278
detection of, in alloys, 279
in minerals, 279
sundry tests for, 278, 279, 280, 281
determination by gravimetric methods:
electrolytic method, 283
metal, precipitation of, 282
determination by volumetric methods:
colorimetric methods, 285
permanganate method, 284
Priester's method, 285
minerals and occurrence of, 278
native, 278
refined, platinum, and palladium in, 457
solubility of, 281
tellurides, 278
wet assay of, 282
Gooch crucible filtration, 59
method for lithium, 477
Thornton method for zinc, 591
preparation of crucible, 58
**Graphite,** 49
in iron, 329
Gravimetric methods, introduction, 3
**Greenockite,** 48
Grinders and pulverizers, 31
Guldberg-Waage's law, 18
Gutzeit apparatus for arsenic determination, 111, 114
method for arsenic, 108 to 114
Gypsum, 49, 168

**Halides,** separation from silver and from silver cyanide, 211
**Halite,** 470
Hanging drop test of fluorine, 260
Hardness of water, determination, 746
**Hematite,** 46, 301
Hempel apparatus, 759
Hesse's law, thermo conserv., 18
Hessite, 517
Hickman, R. E., on iridium, 297
on osmium determination, 421
Holloway-Eschka method for mercury, 384
Horse-power, 848
**Huebnerite,** 602
Hurley's colorimeter, 323
Hydrochloric, arsenic in, 112
acid, commercial anaylsis, 674
free, detection of, 207
purification of, 110, 111
test for iron, 302
detection of, 198
determination of, 198, 199
**Hydroferro** and hydroferri cyanides, determination of, 200
**Hydrofluoric** acid method for alkalies, 475
**Hydrogen,** chapter on, 278 to 289
occurrence of, 287
determination in steel, 287
peroxide test for chromium, 218
sulphide action on rhodium, 492
sulphide, available, 549
sulphide in water, 743
sulphide method for cadmium, 161
sulphide reagent, 783
reduction of copper, 257
sulphide reduction of iron, 309
sulphide test for osmium, 421
sulphide test for palladium, 430
sulphide test for platinum, 449
sulphide test for selenium, 500
sulphide test for tellurium, 500
sulphide test for vanadium, 624
Hydrometer method for determining specific gravity, 766

Ignition, directions for, 61
Ignitions, procedure in, 63
Ilemnite, 46
Indicators in acidimetry and alkalimetry, 661
comparative table of, 662, 663
for end-point detection, 5
preparation of, 798
Industrial products and raw materials, *see* in each chapter on elements, 272, 296, 380, 394, 408, 456, 515, 553, 583, 650, etc.
Inlet gases, $SO_2$ in, 556
Inorganic acids, *see* acids
Instruction, laboratory, 71
Interconversion table, 842
Interpretation of water analysis, 749
Introduction, 3
Iodate, detection of, 290
method for cerium, 204
Iodide, detection of, 290
method for chromium, 224
method for copper, 253, 254
methods — *see* also potassium iodide
Iodine, chapter on, 290 to 296
decomp. iodide by ferric salts, 294
by nitrous acid, 295
detection of, 290
free, 290
iodate, 290
iodide, 290
determination by gravimetric methods as:
palladous iodide, 292
silver iodide, 292
determination by volumetric methods, 293
ferrous salts, 294
Fresenius method, 295
nitrous acid method, 295
Volhard's method, 296
in mineral waters and brines, 296
occurrence of, 290
preparation of sample, 291
free, 291
iodates, 291
iodides, 291
minerals, 291
separation from heavy metals, 291
standard solutions, prep., 782
*see* also in chapter on Iodine
method for tin, 577
Iridium, chapter on, 297 to 300
detection of, 297
by ammonium chloride, 297
caustic alkalies, 297
hydrogen sulphide, 298
other methods, 297, 298
determination by gravimetric methods as:
metal by reduction with zinc, 300
residue, 300
salt ignition, 300
occurrence of, 297
preparation of sample, 299
separation from platinum, 299
Iron, 50
chapter on, 301 to 335
detection of, 302
distinction of ferrous and ferric, 302
methods of, 302
determination by gravimetric methods as:
cupferron precipitation as, 308
oxide of iron, 307
determination by volumetric methods, 309 to 324
oxidation methods, determination with:
dichromate, 312, 315
permanganate, 319, 321
reduction methods, determination with:
stannous chloride, 322
in aluminum, 87
lead, 354
slags, 692
titaniferous ores, 599
water, 739
isolation of, 306
metal, determination of:
carbon in, 327, 328
ferric iron in, 322
graphite in, 329
manganese in, 330–331
by bismuthate method, 331
lead oxide method, 330
persulphate method, 330
phosphorus in, 332
silicon in, 335
sulphur in, 333
minerals and occurrence of, 301
native, 301
preparation and solution of sample, 304
ores of, 304
salts of, 304
sulphides, 304
soluble in aluminum ores, 85
standard solution of, 780
and aluminum separation from chromium, 221
oxide and aluminum in silicate of soda, 515
and alumina in sand, 516
salts, free acid in, 681

Iron and steel, analysis of, 325 to 335
chromium determination in, 221
phosphorus in, 438
steel and alloys, detection of in, 603

Jackson's turbidimeter table, 724, 725
Jolly's method for thorium, 567
Jones' reductor, 319
Jones' reductor in Mo determination, 393
Joule, 848
law, 19

**Kainite,** 460
Knorr arsenic distillation apparatus, 102

Lacmoid indicator, 663, 799
Latent heat, 847
Lavoisier-Leplace's law, 18
Laws and hypotheses, list of, 17
**Lead,** chapter on, 336 to 358
detection of, 337
determination by gravimetric methods as:
chromate, 342
electrolytically, 344
molybdate, 343
sulphate, 341
determination by volumetric methods:
colorimetric method, 358
chromate-iodide method, 345
molybdate method, 347
permanganate method, 348
determination of small amounts, 356, 358
methods for isolation, 340
minerals and occurrence of, 336
native mineral, 336
pig, complete analysis of, 350
preparation and solutions of sample, 339
alloys, 339
oxides, 339
silicates, 339
slags, 339
sulphides, 339
reduction of in fire assay, 703, 704
Lead acetate method for vanadium, 632
reagent for Mo determination, 391
standard solution of, 784
test for chromium, 218
Lead arsenate, 99
Lead bullion, bismuth in, 138
fire assay of, 714
Lead molybdate method for Mo, 391
oxide method for manganese, 330
sulphate in S determination, 539
Leaks, tests for gas, 289
**Lepidolite,** 476
Lessen-Baker iodide method for tin, 577
Liebig bulb, 181
Liebig's method for hydrocyanic acid, 199
**Lime,** fixation of boron, 145
in slags, 691
**Limonite,** 302
**Linnaeite,** 230
**Litharge** in fire assaying, 698, 705
**Lithium,** chapter on, 476 to 480
detection of, 476
determination as chloride, 479
determination as sulphate, 479
determination by Gooch method, 477
determination by Rammelsberg method, 478
determination by spectroscope, 479
minerals and occurrence of, 476
**Litmus** indicator, 662, 663
preparation of solution, 798
Long pile and alternate shovel sampling, 27
Low, A. H., demonstration method of, 71
flask, 42
method for lead, 348
on uranium determination, 617
on zinc determination, 648
Lunge-Ray pipette, 670
Lux, 847

**Magenta** test for bromine, 153
**Magnesia** mixture, preparation of, 784
**Magnesite,** 45, 359
**Magnesium,** chapter on, 359 to 366
detection of, 359
determination, gravimetric, 361
determination, volumetric, 366
in water, 740
minerals and occurrence of, 359
sodium and potassium, determination of, 480
oxide in sand, 516
in silicate of soda, 515
in slags, 694
pyroarsenate, determination of arsenic, 104
pyrophosphate method for phosphorus, 440
**Magnetite,** 46, 301
**Malachite,** green copper carbonate, 240
**Manganese,** chapter on, 367 to 380
detection of, 367
determination by gravimetric methods, 373
by separation as dioxide, 371
determination by volumetric methods:
ammonium persulphate method, 378
bismuthate method, 374
oxalic acid method, 380
oxidation by red lead, 376
Volhard's method, 377
determination in iron and steel, 330

Manganese — determination in lead, 355
determination in ores, oxalic acid method, 72
determination in slags, 693
determination in soils, detection of, 368
determination in Spiegel iron, 380
minerals and occurrence of, 367
ores of, 369
preparation and solution of sample, 369
separations, 369, 370
alloys analysis, 369
basic acetate separation from iron and alumina, 370
dioxide precipitation of, 371
dioxide test for HCl, 207
pyrophosphate method, 373
**Manganite,** 367
Manipulations, general directions for sampling, 20
**Mannite** reagent, 149
**Mannitol,** in boron determination, 148
**Marcasite,** 301
Mariotte's law, 17
Marsh method for arsenic, 109
Marsh tests for arsenic and antimony, 98
Mass action, law of, 18
Measurements of areas and volumes, 846
Meker burner, 61
Melting points, table of, 817
Mendeleeff's periodic law, 18
Mercuric chloride paper, 784
sensatized paper, 109
cyanide test for palladium, 430
**Mercury,** 50
chapter on, 381 to 386
apparatus for determination of, 385
detection of, 381
determination by gravimetric methods:
ammonium sulphide method, 383
electrolytic method, 384
Hollaway-Eschka method, 384
determination by volumetric method of:
Seamon, 386
minerals and occurrence of, 381
native, 381
preparation and solution of the sample, 383
test for osmium, 422
nitrate or silver nitrate test for chromium, 218
Merwin and Stieger's method for fluorine, 267
Metallic lead, analysis of, 350 to 355
Meters for gas measurement, *see* chapter on gas analysis, 757
**Methyl** alcohol, 149
borate, 145
borate, apparatus for, 146, 147, 150
orange indicator, 662, 663
orange, preparation of solution, 798
red solution, 785
red indicator, 663
**Millerite,** 49
Mine gases, analysis of, 768
Mine mill samples, V determination in, 631
Minerals and ores, types and rules for solubility, 45 to 53
iodine in, 291
*see* list at beginning of each chapter
test for gold in, 279
Mineral waters, iodine in, 296
**Millerite,** capillary pyrites, 398
**Mirabilite,** 470
Mohr's alkalimeter, 194
method for chlorine, 215
method for gold, 285
Moisture, method for determining, 65, 66
determination in air, 769
determination in coal, 722
determination in gases, 68
**Molybdate** reduction — permanganate method, phosphorus in iron and steel, 332
**Molybdenite,** 48, 387
molybdenum in, 394
**Molybdenum,** chapter on, 387 to 397
detection of, 387, 388
determination by gravimetric method, 391
determination by volumetric method:
Jones' reductor method, 393
determination in presence of V, 396
in steel, 390
minerals and occurrence of, 387
preparation and solution of sample, 389
separation from V and W, 392
wulfenite and molybdenite, analysis of, 394
**Molybdite,** 46, 387
**Monazite** sand, thorium in, 568
solution of by:
potassium acid sulphate, 564
sulphuric acid extraction, 565
Morphine test for titanium, 587
Moulds for fire assay, 702
Muffle furnaces, 699, 700, 701
Mulligan, J. J., methods, 138, 139
Multiple proportion, law of, 18
Muriatic acid, analysis of, 674

Native gold, 49, 278
iron, 50, 301
mercury, 381
platinum, 50, 448
Nessler's solution, 785

Neuman-Kopp's law, 18
New Jersey Zinc Co., method for Zn, 643
**Niccolite,** copper nickel, 398
**Nickel,** chapter on, 398 to 409
detection of, 398
determination by gravimetric method, 402
dimethylglyoxime method, 402
determination by volumetric method, 406
in alloys, 408
in nickel-plating solution, 408
in ores, 400
minerals and occurrence of, 398
preparation and solution of sample, 400
Nickel-plating solution analysis, 408
**Nitrates,** gravimetric and volumetric methods for, 419
**Nitre,** 460
**Nitric acid,** arsenic in, 112
detection of, 411
determination as nitron nitrate, 414
**Nitrites,** Buvold's method for, 419
Nitrites, water soluble, 420
water insoluble, 420
**Nitrogen,** chapter on, 410 to 420
detection of, 411
detection of in gas, 411
in organic nitrogen, 411
in soils, determination of, 415
of nitrates and nitrites, 417
occurrence of, 410
combined, determination of, 413
Nitrometer method for nitrogen determination, 417
Nitron nitrate method for nitric acid, 414
**Nitrous acid,** detection of, 412
decomp. iodide, 295
Normality factors, calculations, 12
standardization against a solid, 13
equivalents, examples of, 13
Normal solutions and equivalents, 9
table of, 9
in acidimetry and alkalimetry, 10
Note books, keeping of, 73

Occlusion of lead, 356
Offerman's method for fluorine, 266
Ohm, 848
Ohm's law, 19
Oil in water, determination, 744
Organic acids, *see* acids
Orifice meter, 758
Orpiment, 48
Orsat apparatus, 759
**Osmium,** chapter on, 421 to 424
detection of, 421
gravimetric methods for, 423
Osmotic pressure, law of, 18
Ovens, drying, 35, 36
Owens, R. Stuart, on thorium, 564 to 570
Oxalate method for determining calcium, 170
for separation of alkaline earths from magnesium and alkalies, 119
Oxidation reduction methods, 7
Oxidation and reduction reactions, examples of, with calculations, 10
Oxide method for zinc, 64
Oxides, types and solubility, 45
**Oxygen,** chapter on, 425 to 428
apparatus for determination of, 425
determination in gas, 427
determination in steel, 425
dissolved in water, 745
in carbon, determination, 328
occurrence of, 425
properties of, 425
Ozone, determination in air, 771

**Palladium,** chapter on, 429 to 432
detection of, 429
methods for determination of, 432
preparation and solution of sample, 431
separation from gold and silver, 431
separation from iridium, 431
separation from platinum, 431
Palladous iodide method, 292
**Paranitrophenol** reagent, 148
Parting flask, 702
Parting in fire assay, 712
**Patronite,** 623
Perchlorate method for potassium, 469
Periodic law, 18
Permanganate method for antimony, 91
for barium, 127
for calcium, 173
for gold, 284
for lead, 348
for molybdenum, 393
for nitrites, 419
for phosphorus, 445
for titanium, 594
for vanadium, 628, 630, 631
standard, *see* potassium permanganate, 789
standardization for copper determination, 254
Peroxide of hydrogen method for titanium, 597
test for thorium, 564
Persulphate method for manganese, 330
Petot formula, 845
Phenacetolin indicator, 799
Phenolphthalein indicator, 662, 663, 798

Phenylhydrazine acetate test for gold, 280
**Phosphate,** arsenic in, 112
disodium hydrogen, test for uranium, 615
magnesium as, 363
method for zinc, 641
rock, analysis of, 173
rock, composition of, 434
**Phosphoric acids,** detection of, 435
metaphosphoric acid, 435
orthophosphoric acid, 435
phosphoric acid, 435
phosphorous acid, 435
pyrophosphoric acid, 435
free, determination of, 447
**Phosphorus,** chapter on, 433 to 447
detection of, 435
determination by gravimetric methods, 439
ammonium phosphomolybdate method, 439
magnesium phosphate method, 440
determination by volumetric methods for, 442
alkalimetric method for, 442
copper alloys, 443
steel, 444
permanganate method for, 445
volumetric determination of free P, 447
in iron and steel, 438
minerals and occurrence of, 433
ores, phos. rock, minerals, solution of, 437
ores with titanium, 438
preparation and solution of sample, 437
method for oxygen determination, 427
Pigments of titanium, analysis of, 601
Pipettes, standardization of, 805
Pitchblend, 614
Pitot tube, 757
Plant ash, alkali in, 463
**Platinum,** 50
chapter on, 448 to 460
care of, 63
detection of, 448
determination by gravimetric methods, 454
weighing as metal, 454
as metal by electrolysis, 455
as salt, 455
industrial assay of ores of, 456
minerals and occurrence of, 448
preparation and solution of sample, 451
ores, 451
platinum scrap, 451
separation from iron, 452
gold, 452
iridium, 299, 453
osmium, 453
palladium, 431, 453
rhodium, 453
ruthenium, 453
with palladium in refined silver, 456
Pliers for assaying, 702
Pollucite, 481
Portland cement, analysis of, 174
**Potassium,** chapter on, 460 to 469
detection of, 460
determination by gravimetric chloroplatinate method, 467
by chloroplatinate Lindo-Gladding method, 468
by perchlorate method, 469
in fertilizers and soils, 462
minerals and occurrence of, 460
solution of sample, 462
-bromate, *see also* bromate
-bromate method for antimony, 93
-cyanide method for nickel, 406
-dichromate, 310, 312
*see also* dichromate
dichromate, 312, 315
-dichromate, preparation of standard, 11, 14, 786
-ferricyanide test for iron, 302
-ferrocyanide test for iron, 302
-ferrocyanide, *see also* ferrocyanide
-ferrocyanide, standard reagent, preparation solution of, 788
-hydroxide, analysis of, 679
-hydroxide, action on rhodium, 492
-iodate method for arsenic, 106
-iodide, *see also* iodide
method for barium, 128
method for determining bromine, 156
method for chromium, 224
method for copper, 253
method for selenium, 504
test for palladium, 430
test for platinum, 449
test for tellurium, 501
nitrate for fire assay, 699
action on rhodium, 492
test for cobalt, 231
permanganate, 311, 317, 319, 321
*see also* permanganate
method for phosphorus, 445
reagent, 10, 13
standards, solution preparation of, 789 to 791
sulphocyanate, *see also* sulphocyanate
test for cobalt, 231

Precipitate, introduction, 3
Precipitates, washing of, 4
Precipitation, directions for, 55
methods, 8
Priester's method for gold, 285
Producer and fuel gases, 767
**Proustite,** 517
Purple of Cassius test for gold, 278
**Pyrargyrite,** 517
**Pyrite,** 49, 301
Pyrogallate of potassium in oxygen, determination in gas, 428
**Pyrolusite,** 367
**Pyromorphite,** 336
Pyrophosphate method for manganese, 367
**Pyrrhotite,** 49, 301

**Quartz,** 45

Rack, hot water, combined carbon determination, 190
**Radium,** chapter on, 482 to 491
apparatus for determining, 482, 484, 485, 486, 488, 489
detection of, 482
determination by bisulphate fusion method, 488
determination by carbonate fusion method, 484
determination by emanation recovery table, 491
estimation by alpha ray method, 483
emanation method, 484
gamma ray method, 489
methods of solution of, 490
Rammelsberg method for lithium, 478
**Reagents,** chapter on, 775 to 799
Listed alphabetically.
The more important reagents are also listed in the Index.
and fluxes for decomposition of substances, 51 to 53
arsenic determination, 108, 109, 110, 111
for fire assaying, 697
oxidizing, 54
preparation of, *see* chapter with alphabetically arranged list, pp. 775 to 797
reducing, 54
Solvents,
Ammonium hydroxide, 52
Ammonium sulphide, 52
Argol, 53
Borax, 53
Charcoal, 53
Iron, 53
Lead, 53
Litharge, 53
Silica, 53
Potassium bisulphate, 53
Potassium carbonate, 53
Potassium cyanide, 53
Potassium hydroxide, 53
Potassium nitrate, 53
Hydrochloric acid, 51, 52
Nitric acid, 51, 52
Aqua Regia, 51, 52
Sulphuric acid, 51, 52
Hydrofluoric acid, 51, 52
Bromine and bromides, 51, 52
Sodium and potassium carbonates, 52
Sodium peroxide, 52
Potassium acid sulphate, 52
Sodium and potassium hydroxides, 52
Ammonium acetate, 52
Sodium bicarbonate, 53
Sodium carbonate, 53
Sodium nitrate, 53
Sodium thiosulphate, 53
Oxidizing agents, 54
Reducing agents, 54
standard solution:
approx. without weighing, calculation of, 6
approx. normal, without weighing, 7
standard, definition of, 15
Realgar, 48
Red lead, oxidation of manganese, 376
Reducing agents test for chromium, 218
agents test for tellurium, 501
of gross sample, 26
Reduction of iron salts, 309, 310
tests for copper, 240
test, rhodium salts, 492
Reductor tube, 393
References, 851
Refined copper, Cu. in, 243
Refractory materials, decomposition of in chromium determination, 219
Reich apparatus for $SO_2$ determination, 554
Reversible reactions, law of, 18
**Rhodium,** chapter on, 492 to 494
detection of, 492
gravimetric method for, 494
preparation and solution of sample, 493
separation from elements, 493
from iridium, 493
palladium, 494
platinum, 493
ruthenium, 494

**Rhodochrosite,** 367
**Roscoelite,** 623
Rosolic acid, preparation of solution, 798
**Rubidium** and caesium, detection of, 481
occurrence of, 481
**Ruthenium,** chapter on, 495 to 498
detection of, 495
gravimetric method for, 498
preparation and solution of sample, 497
separations, 497, 498
separation from iridium, 497
from osmium, 498
platinum, 497
rhodium, 498
**Rutile** (Nigrine), 46, 586

**Salt,** standard solution, 527
Sample, amount to be taken, 44
Sampling, apparatus for, 32
general directions for, 20
unit, 20
**Sand,** analysis of for commercial value, 516
**Scheelite,** 602, 603
Schmitz, B., on magnesium, 363
Schroetter's alkalimeter, 194
Scorification assay, 709
Scott's apparatus for $SO_2$ determination, 558
apparatus for gas analysis, 558
evolution flask for S determination, 548
method for determining uranium, 620
weighing tube, 673
Seamon's method for mercury, 386
**Selenium** and Tellurium, chapter on, 499 to 507
detection of, 499
Selenium, detection of, 500
commercial, determination of, 506
Selenium and tellurium, determination, gravimetric methods for, 504
sulphur dioxide precipitation, 504
Selenium determination, volumetric, potassium iodide method for, 504
Selenium and Tellurium separation from:
alkalies and alkaline earths, 502
cadmium, copper and bismuth, 503
iron and zinc groups, 502
silver and gold, 503
solution of sample, 502
occurrence of, 499
oxychloride method for Te and Cb, 562
Seller's apparatus for tin, 579
**Senarmontite,** 46
Separation, difficulty of, 16
Separations, *see* under list of each chapter
**Siderite,** 302
**Silica,** determination of, 513
true, determination of, 513
in aluminum ores, 85
in sand, 516
in slags, 691
in sodium silicate, 515
in water, 738
Silicate of soda, analysis of, 515
Silicates, alkalies in Smith method, 473
decomposed by acids, 508
undecomposed by acids, 508
typical list of, 47
**Silicon,** chapter on, 508 to 516
detection of, 509
determination, gravimetric method of, 513
(graphitic) in aluminum, 87
in iron and steel, determination, 335
in sand, analysis of, 516
in silicate of soda, analysis of, 515
minerals and occurrence of, 508
preparation and solution of sample, 510
fluoride decomposition, 515
general considerations, 510
silicates decomposed by acids, 511
silicates undecomposed by acids, 511
properties of, 508
rapid foundry method for, in iron, 335
**Silver,** 50
chapter on, 517 to 530
detection of, 518
chloride method, 518
wet method, 518
determination by gravimetric methods as:
chloride, 520
cyanide, 522
electrolytic, 522
determination by volumetric methods by:
Gay-Lussac method, 524
U. S. Mint method, 527
Volhard's thiocyanate method, 523
determination of in lead, 350
fine, method for, 529
interfering elements, 529
minerals and occurrence of, 517
native, 517
glance, 517
refined, platinum and palladium in, 456
bromide method for determining bromine, 155
bullion, fire assay of, 716
chloride, 210
chloride method for chlorine, 211

Silver—chromate method for chlorine, 215
iodide method for iodine, 292
nitrate test for bromine, 153
chlorides, 207
thiocyanate-ferric-alum method for chlorine, 214
bromine, 156
**Slag** analysis, chapter on, 690 to 696
analysis for:
alumina, 693
copper, 695, 696
iron, 692
lead, 696
lime, 692
magnesia, 694
manganese, 693
silica, 691
zinc, 694
composition of, 690
blast furnace, copper and lead blast furnace slags, 690
decomposition of:
chilled blast furnace, 691
general reverberatory, 691
lead in, 339
Slimes, copper anode, platinum in, 457
**Smaltite,** 230
Smith, J. Lawrence, method for alkalies, 473
**Smithsonite,** dry bone, 636
Snake weighing tube, 672
**Soda** nitre, 470
**Sodium,** chapter on, 470 to 475
detection of, 470
methods for determining, 472
determination as sodium chloride, 472
as sodium sulphate, 472
difference method, 473
minerals and occurrence of, 470
preparation and solution of sample, 471
potassium and lithium, determination of, 480
potassium determination by indirect method, 480
potassium and magnesium, determination of, 480
and potassium in water, 741
carbonate amount for fire assay, 706
carbonate or bicarbonate fusion of silicates, 511
carbonate standard preparation of, 664
fluoride analysis of, 273
hydroxide, analysis of, 677
hydroxide for boron determination, 148
hydroxide standard solution, 793
*see also* chapter on acids
peroxide fusion chrome ores, 220
peroxide test for iron, 303
thiosulphate determination of Mo, 388
standard solution, preparation, of, 794
test for aluminum, 76
Soils, alkalies in, 462
**Solder,** antimony in, 95
Solids, sampling of, apparatus, 24
Solution, apparatus used, 42
Solvents, *see* Reagents also, 51–53
Specific gravity by hydrometer, 675
determination of, 848
of gases, table, 819
Specific heat, 847
Spectra of strontium, 532
Spectroscopic method for determining lithium, 479
test for thorium, 564
**Spelter,** cadmium in, 164
**Sphalerite,** zinc blend, 48, 448, 636
Spiegel iron, manganese in, 380
**Spodumene,** 476
Stains, standard for arsenic, 109
Standard, ultimate, preparation of, 664
Stannic acid method for bichloride of tin determination, 583
**Stannite,** 571
Stannous chloride method for iron, 322
reduction of iron, 313, 315, 322
solution, 796
test for osmium, 422
**Steel,** analysis of, *see* iron
iron, etc., copper in, 258
detection of V in, 624
chromium in, 228
cobalt in, 237
copper in, 259
hydrogen in, 287
manganese in, 374, 375
molybdenum in, 390
oxygen in, 425
phosphorus in, 444
sulphur in by evolution, 547
vanadium in, 634
solubility of, 50
Stetser and Norton combustion apparatus, 187
combustion, train for carbon determination, 186
Stieger and Merwin method for fluorine, 267
**Stibnite,** 48, 89
**Strontianite,** 45, 531

**Strontium,** chapter on, 531 to 535
detection of, 531
determination by gravimetric method, 535
oxide method, 535
sulphate method, 535
determination by volumetric methods, 535
alkalimetric method, 535
preparation and solution, 533
minerals and occurrence of, 531
separation from alkalies, 533
barium, 534
calcium, 533
magnesium, 533
Sulphocyanate test for cobalt, 231
Suggestions, 69
experimental work in Al analysis, 76
**Sulphate** in water, 740
Sulphate method for barium, 123
method for cadmium, 162
method for zinc, 64
procedure for separation of alkaline earths from magnesium and alkalies, 120
test for strontium, 531
Sulphates, types and solubility, 49
Sulphates, water soluble, 540
**Sulphide,** ammonium or hydrogen test for V, 624
method for bichloride of tin determination, 585
Sulphides, lead in, 339
sulphur in, 547
typical examples of, 47, 48
Sulphocyanate test for iron, 302
**Sulphur,** 50
chapter on, 536 to 558
available in brimstone, 553
detection of, 537
element, 537
sulphates, 537
sulphides, 537
sulphites, 537
thiosulphates, 537
determination, gravimetric methods by:
Barium sulphate method, cold solutions, 544
Barium sulphate method, hot solutions, 542
Preliminary remarks on proportion, 542
determination, volumetric method by:
evolution method, 547
in cinders, 547
in iron and steel, 333, 547
evolution method, 333
gravimetric method, 334
industrial products and raw materials:
brimstone, analysis of, 553
sulphuric acid gases, 554
occurrence of, 536
element, 536
hydrogen sulphide, 536
sulphate ores, 536
sulphide ores, 536
sulphur dioxide, 536
preparation and solution of sample
element, 538
barium and lead sulphate, 539
coal, Eschka's method, 539
ores, 538
rocks, silicates, etc., 539
substances containing iron, 540
sulphates, sulphides, sulphites, 538
thiosulphates, 538
water soluble sulphates, 540
separation from:
ammonium and alkali salts, 541
metals forming insoluble salts, 541
nitrates and chlorides, 541
silica, 541
volatile in coal, 723
free, determination of, 552
dioxide detection of molybdenum, 388
detection of palladium, 429
method for selenium, 500
test for titanium, 587
**Sulphuric** acid, analysis of, 676
arsenic in, 99, 112
combined in silicate of soda, 515
gases, 554
burner gases, $So_2$ in, 554
exit gases, $SO_2$ in, 555
inlet gases, $SO_2$ in, 556
standard preparation of, 665, 795
*see* acidimetric chapter
**Sulphurous** acid, reduction of iron, 310

**Tantalum** and columbium, chapter on, 559 to 563
detection of, 559
method for, 562
Tantalum, minerals of, 559, 561
Tantalum and columbium, preparation and solution of sample:
minerals, 561
oxides, 561
separation from antimony, silica, tin, tungsten, 562
separation from one another, 562
**Tellurite,** 46

**Tellurium,** detection of, 500
commercial, determination of, 507
method for determination, 505
occurrence of, 499
Temperature standards table, 817 to 818
Test lead, reduction of iron with, 310, 314
**Tetrahedrite,** gray copper ore, 240
Thiocyanate method for copper, 243
method for silver, 523
test for silver, 518
*see also* sulphocyanate
Thiosulphate method for iodine, 293
of sodium, detection of Mo, 388
standard solution, *see* sodium thiosulphate, 794
Thomson's acidimetric table of indicators, 662
**Thorite** (silicates), solution of, 564
**Thorium,** chapter on, 564 to 570
detection of, 564
determination by gravimetric method, 567
determination, Jolly's emanation method, 567
in monazite sand, 568
minerals and occurrence of, 564
preparation and solution of sample, 564
gas mantles (oxides), 565
phosphates (monazite, etc.), 564
silicates (thorite, etc.), 564
properties of, 565
**Tin,** chapter on, 571 to 585
detection of, 571
determination in alloys, 576, 581
determination in bichloride of tin, 583 to 585
determination, gravimetric methods:
bichloride of tin, 583
Acker's method, 583
stannic acid method, 584
sulphide method, 585
determination by volumetric methods, 577 to 582
Lessen-Baker iodide method, 577
minerals and occurrence of, 571
preparation and solution of sample:
sodium carbonate method, 574
sodium cyanide method, 573
separation from:
antimony, copper and lead, 574
aluminum, iron, phosphorus and tungsten, 575
Titaniferous ores, analysis of, 599
aluminum in, 600
iron in, 599, 600
phosphorus in, 600
titanium in, 599
**Titanium,** chapter on, 586 to 601
detection of, 587
determination, gravimetric method:
Gooch-Thornton method modified, 591
determination volumetric methods:
colorimetric-peroxide method, 597
reduction-ferric method, 595
reduction-permanganate method, 594
minerals and occurrence of, 586
preparation and solution, 588
alloys, 589
element, 588
ores, 589
oxides, 588
salts, 588
slags, titaniferous, 589
steel, 588
separation from:
alkaline earths, 590
aluminum and iron, 590
cobalt, manganese, nickel, zinc, 590
ferro-carbon titanium analysis, 593
Titanium, in ores, titaniferous, 599, 613
in pigments, 601
Titration of acids and alkalies, 669
Tolerances and precision of weights, 815
**Tourmaline,** 143
Traces of antimony, detection of, 89
determination of, 96
of arsenic, Gutzeit method, 108
of chromium, 228
of iron, 87, 302
*see also* detection under elements in each chapter
Triangles, pipestem for tripods, 63
**Tungsten,** chapter on, 602 to 613
detection of, 603
determination by gravimetric methods:
in alloys and steel, 606, 608
ferro and metallic tungsten, 609
determination by volumetric method, 613
determination in ores and concentrates, 610
Tungsten, isolation of, 611
minerals and occurrence of, 602
separation from:
silica, 604
tin, 605
titanium, 605
solution of sample acids, minerals, oxides, 604
Watts's aqua regia method, 613
**Tungstite,** 46

Turmeric paper, preparation of, 799
Type metal, analysis of, 683 to 685

**Ulexite,** boranatrocalcite, 143
Units, comparison tables, areas, avoirdupois weights, capacities, length, masses, volumes, 841
Uraninite, 614
**Uranium,** chapter on, 614 to 622
detection of, 614
uranous salts, 614
uranyl salts, 615
determination by gravimetric methods, 617
Low's method, 617
Scott's glacial acetic method, 619
determination by volumetric method, 622
minerals and occurrence of, 614
preparation and solution of sample element, 616
ores, oxides, carnotite, 616
U. S. Bureau of Standards methods for:
manganese in steel, 331
silicon in steel, 335
sulphur in steel, 334
U. S. Mint method for fire assay, 717
method for silver, 527
Useful data, tables of, 816

Vamari-Mitscherlich-Devarda method for nitrogen, 415
apparatus for nitrogen determination, 415
**Vanadinite,** 623
**Vanadium,** chapter on, 623 to 635
detection of, 624
detection in steel, 625
detection and comparison with chromium, 624
determination by gravimetric lead acetate method, 627
determination, volumetric by:
permanganate-hydrogen sulphide m., 628
permanganate-sulphur dioxide m., 628
permanganate-zinc method, 630
determination in presence of Mo, 396
minerals and occurrence of, 623
preparation and solution of sample:
alloys, 626
element, 626
ores high in silica, 626
ores low in silica, 626
oxides and salts, 626
special procedures, determining:
vanadium, arsenic and antimony, 633
vanadium and chromium, 634
vanadium and iron, 634
vanadium and molybdenum, 633
Vanier bottle, 182
Vapor tension of water, table, 820
Volhard's method for bromine, 156
method for chlorine, 214
method for hydrocyanic acid, 199
method for iodine, 296
method for manganese, 377
thiocyanate method for silver, 523
Volt, 848
Volume and weight conversion table, 844
Volumes of solids, formulæ, 846
Volumetric apparatus, standardization of, 64
precautions in analysis, 64
methods, introduction, 5
classification of, 5

Washing of precipitates, 59
**Water** analysis, chapter on, 736 to 753
determination of:
acidity, 742
alkalinity, 741
aluminum, 739
ammonia, 743
calcium, 739
carbonic acid, free, 742
chlorine, 743
corrosion action, 750
foaming and priming, 750
hardness, 746
hydrogen sulphide, 743
iron, 739
magnesium, 740
mineral, total, 748
oil, 744
oxygen, 745
scale forming sub., 751
silica, 738
sodium and potassium, 741
sulphate, 740
table of separations, 737
determination in materials, 65, 66
hypothetical combinations, 752
mineral analysis of, 737
Watt, 848
Watt-hour, 848
Watts's aqua regia method for tungsten, 613
**Wavellite,** 433
Weighing, 37
balance, use of, 37
care of balance, 39
rules for weighing, 40
Weight, checking of, 41
Weights, standardization of, 64, 811

Welch and Weber on detection of tin, 572
Welsbach mantles, cerium in, 205
Wet meter, 757
**Willemite,** electric calamine, 636
**Witherite,** 45, 115
analysis of, 129
**Wolframite,** 602
**Wulfenite,** 387
molybdenum in, 394

**Zinc,** chapter on, 636 to 654
detection of, 637
determination by gravimetric methods by:
electrolytic method, 642
oxide method, 641
phosphate method, 641
sulphate method, 641
determination by volumetric methods by:
ferrocyanide, interior indicator, 643
ferrocyanide, exterior indicator, 648
determination in lead, 355
in slags, 694
determining traces of, 654
methods, preparation and solution of sample, 638
general procedure, 639
carbonaceous material, 639
metallic material, 639
ores, 638
refractory material, 639
salts, 638
zinc pulp, 638
minerals and occurrence of, 636
properties of, 637
pulp, moisture in, 638
reduction of iron with, 310, 319
separation as sulphide, notes on, 646
separation from Al, Fe, Mn, Ni, Co, etc., 640
test for osmium, 421
**Zincite,** 46
red zinc ore, 636
blend, 48, 448, 636
**Zircon,** 655
**Zirconium,** chapter on, 655 to 659
detection of, 655
methods of determination as:
oxide, 659
phosphate, 658
conditions of accuracy, 658
methods, preparation and solution of sample:
minerals, oxides, etc., 657
silicious materials, 657
minerals and occurrence of, 655

# LITERATURE OF THE CHEMICAL INDUSTRIES

On our shelves is the most complete stock of technical, industrial, engineering and scientific books in the United States. The technical literature of every trade is well represented, as is also the literature relating to the various sciences, including books useful for reference as well as those fitted for students' use as textbooks.

A large number of these we publish and for an ever increasing number we are the sole agents.

ALL INQUIRIES MADE OF US ARE CHEERFULLY AND CAREFULLY ANSWERED AND COMPLETE CATALOGS AS WELL AS SPECIAL LISTS SENT FREE ON REQUEST

D. VAN NOSTRAND COMPANY

*Publishers and Booksellers*

8 WARREN STREET NEW YORK

LIBRARY
WITHDRAWN
from
Funderburg Library
MANCHESTER COLLEGE

543.6 Sco86 c.1
Scott, Wilfred Welda 150101 000
Technical methods in analysis
3 9315 00047587 8
MANCHESTER COLLEGE LIBRARY

543.6
Sco86
Scott
Technical methods in analysi
of metallurgical & allied
products
NOV 2 '7 16255

543.6
Sco86
9266

# Manchester College Library

## RULES

1. Books of fiction may be kept two weeks and may be renewed once for the same period. The time limit for books of non-fiction shall be determined by the librarian.

2. A fine of a cent a day shall be charged on each book kept overtime, except reserved books. A fine of two cents per hour will be charged for reserved books which are not returned at the time specified by the librarian when the book is taken. No book will be issued to persons incurring such fines until they have been paid.

3. All injuries to books beyond reasonable wear and all losses shall be made good to the satisfaction of the librarian.